

## 4. SAMPLING AND ANALYSIS METHODS FOR PARTICULATE MATTER AND ACID DEPOSITION

### 4.1 INTRODUCTION



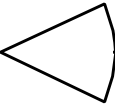
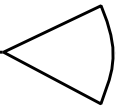
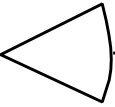

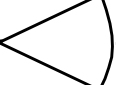


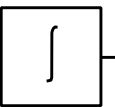
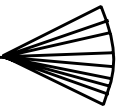





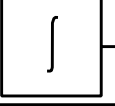
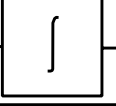

Assessment of health risks associated with airborne aerosols implies that measurements be made defining the aerosol characteristics, concentrations and exposures that contribute to, or simply correlate with, adverse health effects. The proper selection of an aerosol sampling or analysis methodology to accomplish such measurements requires that rationales be applied that consider how the resulting data will be used and interpreted, in addition to the data quality required. As an example, treatment of a sample to remove particle-associated liquid water, either by heating the sample during the collection process or by equilibrating the sample at a low relative humidity subsequent to collection, may lead to changes in the character of the collected particles, relative to the dispersed particles, in addition to the removal of water (e.g. Meyer et al., 1995). Similarly, integrated collection of acidic fine aerosols, without selectively removing the larger, more basic particles, will cause neutralization (i.e., modification) of the sample on the substrate (Stevens et al., 1978). The same logic applies to the selective removal of gas phase components during sampling that might react with the deposited aerosol sample, in a manner inconsistent with naturally occurring transformation processes. The assumption that fixed-location measurements are representative of inhalation exposure implies that the effects of local spatial and temporal gradients are understood and appropriately applied to the sampler siting criteria (Spengler et al., 1994). Development of relationships between aerosol characteristics and health or ecological responses requires that the aerosol sampling and analysis processes are truly representative and adequately defined.

The application of sampling and analytical systems for aerosols must recognize that particles exist modally as size distributions generated by distinctively different source categories and having distinctly different chemistries, as discussed in Chapter 3. Two important reasons for making size-specific aerosol measurements are (a) to relate the in situ aerosol character to the potential deposition sites, and thus toxicity, of the respiratory system, and (b) separation of the size distribution modes to identify sources, transformation processes or aerosol chemistry. The interpretation of particle size must be made based on the diameter definition inherent in the

measurement process. Since the respiratory system classifies particles of unknown shapes and densities based on aerodynamic diameter, elucidation of aerosol relationships with health responses requires that sampling techniques either incorporate inertial aerodynamic sizers or provide mechanisms to accurately convert the measured diameters (e.g., optical) to an aerodynamic basis. All particle diameters described in this chapter are aerodynamic, unless otherwise specified.

Friedlander (1977) provided the descriptive matrix shown in Figure 4-1 for placing measurement techniques that define aerosol characteristics into perspective, in terms of their particle sizing capabilities, resolution times and chemical identification attributes. This approach defined these characteristics by resolution (single particle or greater), discretizing ability, and averaging process. The author notes that the "perfect" aerosol sampler would characterize particle size with "perfect" resolution, determine the chemistry of each particle "perfectly", and operate in real-time with no "lumping" of classes. These characteristics could be amended in "real-world" terms by suggesting that the "perfect" sampler would also have minimal cost and operator intervention. Also, if the aerosol measurement design goal is to mimick the respiratory system, physiological averaging characteristics must be considered. Size-specific, integrated aerosol measurements have improved significantly and their capabilities are better characterized since the 1987 PM<sub>10</sub> NAAQS, but a "perfect" aerosol sampling system has not been devised. As discussed below, the methodologies required to adequately define the performance specifications of aerosol samplers have yet to be devised.

Many recent developmental efforts in aerosol measurement technologies have addressed the need to perfect the chemical characterization of reactive or volatile species collected on filtration substrates (e.g., Lamb et al., 1980; Koutrakis et al., 1988). Some of the most significant recent advances in aerosol measurement technologies have come in the form of analysis system "protocols", rather than individual pieces of hardware. Recognizing that there is no single "perfect" sampler, these protocols attempt to merge several aerosol sampling and analysis technologies into an adaptable and analytically versatile system. System attributes typically include one or more size-specific aerosol inlets, subsequent fractionators to separate the fine and coarse particle modes, and denuders and/or sequential filter packs to selectively account for reactive gas phase species. Examples include EPA's

Instrument	Resolution			Quantity Measured (Integrand x $N_{\infty}^1$ )
	Size	Time	Chemical Composition	
Perfect Single Particle Counter Analyzer				$g$
Optical Single Particle Counter				$\int_{v_1}^{v_2} g \, d\eta \, dv$
Electrical Mobility Analyzer				$\int_{v_1}^{v_2} g \, d\eta \, dv$
Condensation Nuclei Counter				$\int g \, dv \, d\eta = 1$
Impactor				$\int_{v_1}^{v_2} g \, d\eta \, dv$
Impactor Chemical Analyzer				$\int_{v_1}^{v_2} g \, \eta_j \, d\eta \, dv$
Whole Sample Chemical Analyzer				$\int \int g \, \eta_j \, d\eta \, dv$

**Key:**

 Resolution of single particle level

 Discretizing process

 Averaging process

**Figure 4-1. Characteristics of aerosol measurement instruments.**

Source: Friedlander (1977).

Versatile Air Pollution Sampler (VAPS) (Conner et al., 1993), the Southern California Air Quality Study (SCAQS) sampler (Fitz et al., 1989) and the Interagency Monitoring of PROtected Visual Environments (IMPROVE) sampler (Malm et al., 1994).

Recognizing that personal exposure concentrations for aerosols may differ from classical outdoor fixed-location measurements has produced much smaller and less obtrusive samplers

using the same sizing techniques for application indoors, or even to be worn on the body during normal activities. Miniaturization of aerosol separators stretches the limits of current technologies to maintain required sampling precisions and accuracies. One of the most significant limitations imposed by the low flowrates inherent in personal exposure samplers is the extremely small sample size available for chemical analysis.

This chapter briefly describes the technical capabilities and limitations of aerosol sampling and analytical procedures in Sections 4.2 and 4.3, respectively, focusing on (1) those that were used to collect data supporting other sections in this document, (2) those supporting the existing  $PM_{10}$ , TSP<sup>1</sup> and Pb regulations, (3) those that were used to support health and welfare response studies, (4) those having application in development of a possible fine particle standard, and (5) discussing the attributes of several new technologies. The discussion of aerosol separation technologies is divided between (a) devices used to mimic the larger particle ( $>10\ \mu m$ ) penetration rationales for the upper airways, and (b) those devices generally used to mimic smaller particle penetration ( $< 10\ \mu m$ ) to the thoracic regions. These device descriptions are followed by sampling considerations for their applications. The applications of performance specifications to define these measurement systems for regulatory purposes are discussed, along with a number of critical observations suggesting that the current specification process does not always ensure the accuracy or representativeness necessary in the field. The EPA program designating  $PM_{10}$  reference and equivalent sampling systems is then briefly described, along with a current list of designated devices. Selected measurement systems used to provide more detailed characterization of aerosol properties for research studies are discussed, with a focus on the determination of particle size distributions.

Aerosol sampling systems for specialty applications, including automated samplers, personal exposure samplers and the sampling systems used in aerosol apportionment studies are briefly described. The chapter then presents a short section (4.4) on sampling and analysis of bioaerosols Nevalainen et al. (1992). Also, Nevalainen et al. (1993), and Qian et al. (1995) provide excellent summaries of the principles involved in bioaerosol sampling and the most commonly used techniques.

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<sup>1</sup>Subsequent identifications in this chapter: “TSP” for Total Suspended Particulates by high volume sampler, “ $PM_{10}$ ” for the fraction less than  $10\ \mu m$ , “fine” for the fraction less than  $2.5\ \mu m$ .

## 4.2 SAMPLING FOR PARTICULATE MATTER

### 4.2.1 Background

The development of relationships between airborne particulate matter and human or ecological effects requires that the aerosol<sup>2</sup> measurement process be accurately, precisely and representatively defined. Improvements in sampling methodologies since the 1982 Air Quality Criteria Document for Particulate Matter and Sulfur Oxides (U.S. Environmental Protection Agency, 1982)<sup>3</sup> was released, have resulted from improved sensor technologies, and more importantly, a better understanding of the aerosol character in situ<sup>4</sup>. Additionally, health studies and atmospheric chemistry research in the past decade have focused more closely on smaller, better-defined aerosol size fractions of known integrity, collected specifically for subsequent chemical characterization.

The system of aerosols in ambient air is a continuum of particle sizes in a gas phase carrier formed as the summation of all size distributions produced by individual sources and secondary transformations. Portions of the composite distributions are often found to exist lognormally (Baron and Willeke, 1993; see also Chapter 3, Section 3.3.3). Aerosol systems also exist as a continuum of particle "ages", resulting from loss and transformation mechanisms such as agglomeration, settling, volatilization, gas-particle reaction, and rain-out affecting freshly generated particles. The chemical compositions of the various portions (modes) of the aerosol size distribution are more discrete, and sampling strategies must consider a specific range of sizes for a given chemical class. The constantly changing character of the atmosphere (or of indoor air) places a premium on sampling strategies both to collect representative aerosol samples from the air and to protect their integrity until analyzed.

The 1982 Criteria Document provided basic descriptions of many aerosol measurement techniques still used today. These included both older optically-based techniques, such as "Black Smoke" or "British Smoke" (BS) or "coefficient of haze" (COH) methods and certain other now lesser used gravimetric methods, that are only briefly mentioned here but not

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<sup>2</sup>Consistent with recent literature (e.g., see Willeke and Baron, 1993), the term "aerosol" will refer to the continuum of suspended particles and the carrier gas.

<sup>3</sup>Referred to in the text subsequently as an entity as the "1982 Criteria Document".

<sup>4</sup>The in situ characteristics of particles in the ambient air medium can be substantially modified by the sampling and analysis processes. For example, a particle counter which draws particles through a restrictive or heated inlet before they reach the sensing volume, may perceive the particle properties (e.g. scattering coefficients, size distributions) differently from those that existed in the ambient.

described in detail. Instead the reader is referred to the earlier Criteria Document (U.S. Environmental Protection Agency, 1982) for more information on those methods not extensively covered here. This section mainly highlights the more recent peer-reviewed research on aerosol measurement technologies since 1982 and notes salient points that should be considered in their application. The aerosol sampling section is not intended to be an exhaustive treatise, but is structured to highlight important concepts and technologies relevant to the development of aerosol measurement/response relationships, or supporting existing and potential EPA aerosol regulations. Ancillary reference texts, describing basic aerosol mechanics (e.g., Hinds, 1982; Reist, 1984) and applied aerosol mechanics and measurements (e.g., Willeke and Baron, 1993; Hering, 1989; Lundgren et al., 1979; Liu, 1976) should be consulted for more fundamental details.

## **4.2.2 Large Particle Separators**

### **4.2.2.1 Cutpoint Considerations**

The collection of an aerosol sample is defined by the penetration characteristics of the inlet, overlaid on the existing in situ size distribution. Cooper and Guttrich (1981) describe this process mathematically, and they estimate the influences of non-ideal penetration characteristics. Miller et al. (1979) described the considerations for the possible selection of 15  $\mu\text{m}$  (designated "inhalable") as a standard for size-selective particle sampling with upper airway respiratory deposition as the primary consideration. The selection of the most appropriate aerodynamic criteria for ambient aerosol sampling was only partially resolved by the 1987 EPA designation (U.S. Environmental Protection Agency, 1987) of a 10  $\mu\text{m}$  ( $\text{PM}_{10}$ ) cutpoint. The "ideal"  $\text{PM}_{10}$  inlet was referenced to the thoracic penetration model of Lippmann and Chan (1979). Ogden (1992) noted that the standardization for aerosol cutpoint sizes and separation sharpness is still under debate across settings (ambient air, occupational) and across national and international governmental entities. As shown in Figure 4-2 (from Jensen and O'Brien, 1993), the international conventions for cutpoints have been roughly categorized as Respirable, Thoracic and Inhalable (previously, Inspirable). These cutpoints are related to the penetration, respectively, to the gas exchange region of the lung, the larynx, and the nasal/oral plane. The influences of physiological variables on these

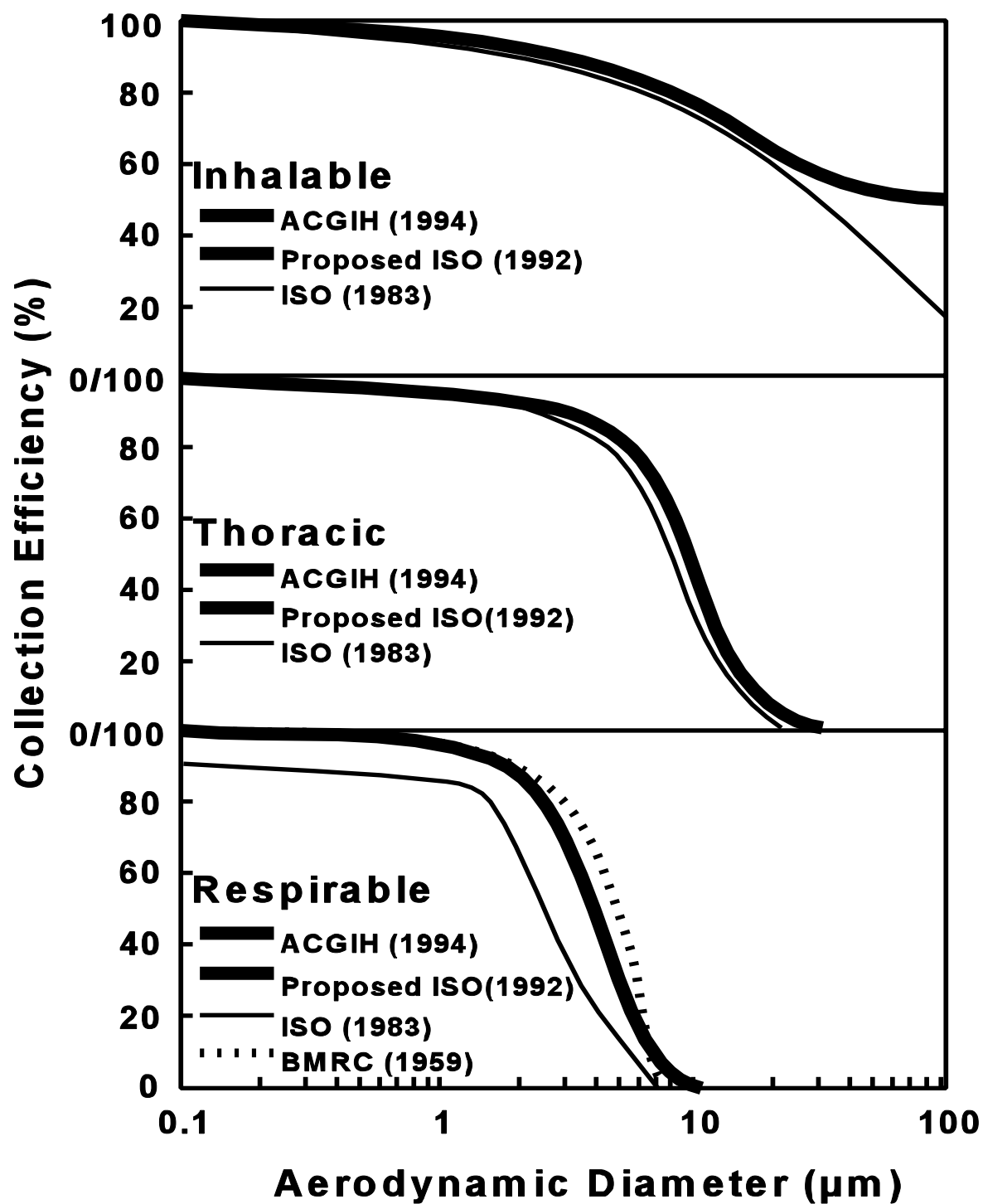


Figure 4-2. American Conference of Governmental Industrial Hygienists (ACGIH), British Medical Research Council (BMRC), and International Organization for Standardization (ISO) size-selective sampling criteria.

Source: Jensen and O'Brien (1993).

cutpoints are described by Soderholm (1989). The British Standard EN 481 (CEN [European Committee for Standardization], 1993) describes size fraction definitions for workplace aerosol sampling, and identifies inhalable "conventions" relative to thoracic, respirable, extra-thoracic and tracheobronchial penetration (but not necessarily deposition) in the respiratory system. They define a thoracic cumulative lognormal distribution with a median of  $11.64 \mu\text{m}$  and a geometric standard deviation of 1.5, such that 50% of airborne particles with  $D_a = 10 \mu\text{m}$  are in the thoracic region. The American Conference of Governmental and Industrial Hygienists (ACGIH, 1994) also adopted these convention definitions. Owen et al. (1992) provides an extensive list of the outdoor and indoor particles by type and source category that are found in or overlap these ranges. Willeke et al. (1992) describe the sampling efficiencies and test procedures for bioaerosol monitors.

The concept of using an inlet or separator that has the same sampling (penetration) characteristics as portions of the respiratory system has been discussed by a number of researchers, including Marple and Rubow (1976), Lippmann and Chan (1979), Vincent and Mark (1981), Soderholm (1989), Lidén and Kenny (1991) and John and Wall (1983). They describe sampler design considerations for matching penetration models for respirable, thoracic and inhalable fractions that have been proposed by a number of governing bodies. Since all models proposed for the same fraction do not necessarily coincide, given the variability and differences in interpretation of respiratory system data, Soderholm (1989) proposed compromise conventions for each fraction. Watson et al. (1983), Wedding and Carney (1983), and van der Meulen (1986) mathematically evaluated the influences of inlet design parameters on collection performance relative to proposed sampling criteria. These analyses suggested that factors such as extremes in wind speed and coarse particle concentration could pose significant problems in meeting performance specifications.

An analysis of the human head as an aerosol sampler was discussed by Ogden and Birkett (1977), who noted that breathing is an anisokinetic sampling process. The concept of a "total inhalable" fraction that passes the oral and nasal entry planes was refined by Mark and Vincent (1986) with the development of a personal aerosol sampling inlet that mimicked this penetration as a function of aerodynamic size. The inlet was designated the IOM for the Institute for Occupational Medicine in Edinburgh, Scotland, where it was developed with the cutpoint as a function of wind speed and aerosol type shown in Figure 4-3. The total



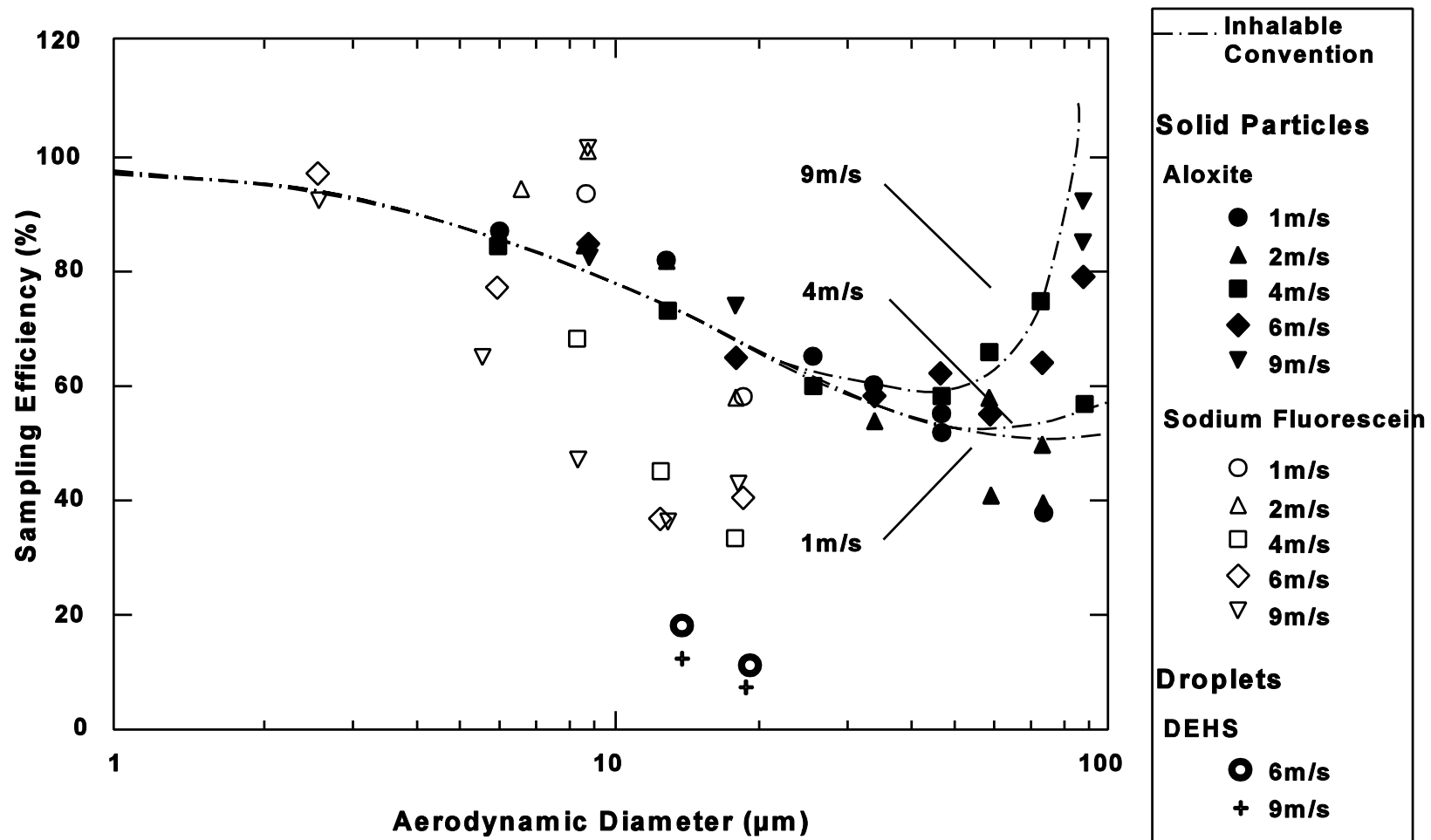


Figure 4-3. Sampling efficiency of IOM ambient inhalable aerosol sampler for three different types of test aerosol.

Source: Mark et al. (1992).

inhalable approach has been adopted by the International Standards Organization (ISO, 1993), European Committee for Standardization (CEN, 1993) and by the American Conference on Governmental and Industrial Hygienists (ACGIH, 1985; ACGIH, 1994) for workplace aerosol sampling. The ACGIH (1985) reference provides a detailed rationale for the selection of various cut sizes. The total inhalable fraction using the IOM inlet was selected for a total human exposure study (Pellizzari et al., 1995) to provide the total body burden for metals (lead and arsenic) by the air exposure route.

Similar thoracic penetration conventions have been adopted by ISO, CEN, ACGIH and EPA, each with  $D_{50}$  values of  $10.0\ \mu\text{m}$  (ISO, 1993; CEN, 1993; ACGIH, 1994; and U.S. EPA, 1987). The EPA definition was based primarily on the data of Chan and Lippmann (1980). The exact shapes of each efficiency curve were mathematically defined by Soderholm (1989) and are slightly different for each convention.

The respirable conventions have had  $D_{50}$  values ranging from  $3.5$  to  $5.0\ \mu\text{m}$ , but a compromise convention has been accepted internationally by several organizations. It has a  $D_{50}$  of  $4.0\ \mu\text{m}$  (Soderholm, 1989). ISO (1993) calls this the "healthy adult respirable convention". Lidén and Kenny (1992) discuss the performance of currently available respirable samplers. EPA's emphasis on the  $2.5\ \mu\text{m}$  cutpoint was more closely associated with separating the fine and coarse atmospheric aerosol modes, rather than mimicking a respiratory deposition convention. The exact location of this minimum in the atmospheric size distribution is currently under debate. It is noteworthy that ISO (1993) defines a "high risk" respirable convention which is claimed to relate to the deposition of particles in the lungs of children and adults with certain lung diseases. The respirable "high risk" convention has a  $D_{50}$  of  $2.4\ \mu\text{m}$ , so it could be identified closely with the EPA samplers having a cutpoint of  $2.5\ \mu\text{m}$ .

The  $\text{PM}_{10}$  size fraction has become nearly universal for ambient air sampling in the U.S., with the implementation of the 1987 standard (U.S. Environmental Protection Agency, 1987). The setting of performance specifications, even with their limitations, has provided a more consistent  $\text{PM}_{10}$  data base, with better definition of the data quality. As additional information becomes available on the sources of biases in aerosol collection methodologies, further characterizations of older methods may be needed to better define the quality of collected data. Factors that affect bias, and especially representativeness, should be identified and their influences determined as a function of particle size. As examples, Appel et al. (1984) studied

gas/particle and particle/substrate interactions for sulfates and nitrates, volatilization losses of nitrates were reported by Zhang and McMurry (1992), while losses for organics were reported by Eatough et al. (1993). Because of the prevalence of these chemical classes in the fine fraction, the effect of the losses on larger fractions (e.g., PM<sub>10</sub>, TSP) would be proportionately smaller and can now be estimated. The losses of larger particles through aerosol inlet sampling lines (Anand et al., 1992) has a substantial influence on PM<sub>10</sub> coarse fraction samples. This was demonstrated for the British smoke shade sampler inlet line by McFarland et al. (1982). Inlet losses would be expected to play only a minor role in sampling the fine particle fraction (<2.5  $\mu\text{m}$ ). Biases in concentration for samplers with large particle cutpoints are exacerbated by the large amount of mass present near the cutpoints and the steep slope of mass versus aerodynamic size. Thus, small changes in cutpoint can give significant and hard-to-predict mass biases.

#### **4.2.2.2 Total Suspended Particulates**

The TSP high volume sampler has remained essentially unchanged since the sampler's identification as a reference ambient sampling device in 1971 (Federal Register, 1971). The sampling performance (e.g., wind speed and direction sensitivity) was described in detail in the 1982 Criteria Document, and the TSP sampler was shown by McFarland and Ortiz (1979) to collect particles with aerodynamic diameters exceeding 40  $\mu\text{m}$ . More importantly, its particle collection characteristics were shown to be significantly sensitive to wind speed (2 to 24 km/h) and wind direction. Only minor technical updates have been incorporated in commercially available units, such as in the types of available sequence and elapsed timers (mechanical, electronic) and in the types of flow controllers (mass flow, volumetric). Also, cassettes are now available that protect the fragile glass or quartz fiber filters during handling and transport. Size fractionating inlets for smaller size cutpoints (e.g., 2.5, 6.0 and 10.0  $\mu\text{m}$ ) and cascade impactors have been developed. Similar to the Pb strategy of using the TSP high volume sampler to collect a "total" sample, asbestos sampling utilizes an aerosol inlet that attempts to collect a "total" sample, by using an open-faced filter holder with a conductive inlet cowling. Baron (1993) discusses the potential anisokinetic problems that can occur with such a simple inlet, but notes that the small Stokes number for typical asbestos fibers provides efficiencies close to 100%.

#### 4.2.2.3 Total Inhalable Particles

The toxicity of contaminants such as lead poses health concerns as total body burdens, suggesting that penetration of all aerosols inhaled into the nose and mouth must be considered, rather than just thoracic penetration. The TSP sampler for atmospheric lead is thought (Federal Register, 1978) to more closely capture this larger size fraction than would a  $PM_{10}$  counterpart, but was not specifically designed to mimic inhalability. The ISO "inhalable" draft sampling convention (ISO, 1993) is intended to apply to such situations, defining collection of all particles passing the oral/nasal entry planes. The total inhalable cutpoint is currently available only in a personal sampler version. Mark and Vincent (1986) described the development of an inhalable particle inlet (designated as the IOM) meeting the ISO (1992), CEN (1993) and ACGIH (1994) conventions for inspirable dust. This inlet was improved by Upton et al. (1992) and tested by Mark et al. (1992) and shown to satisfy the ACGIH criteria for wind speeds of 0.5 and 1.0 m/s.

#### 4.2.2.4 $PM_{10}$

The penetration of ambient aerosols through a size-fractionating inlet to the collection substrate must be characterized over the ranges of operating conditions (meteorology and aerosol types) that may be encountered. The range of conditions currently required by EPA  $PM_{10}$  performance specifications was given in U.S. Environmental Protection Agency (1987). Ranade et al. (1990) and John and Wall (1983) described the required testing, which specifies a controlled flow wind tunnel, monodispersed fluorescently-tagged wet and dry aerosols, and an isokinetic nozzle aerosol sampling reference to determine aerodynamic penetration through candidate  $PM_{10}$  inlets.

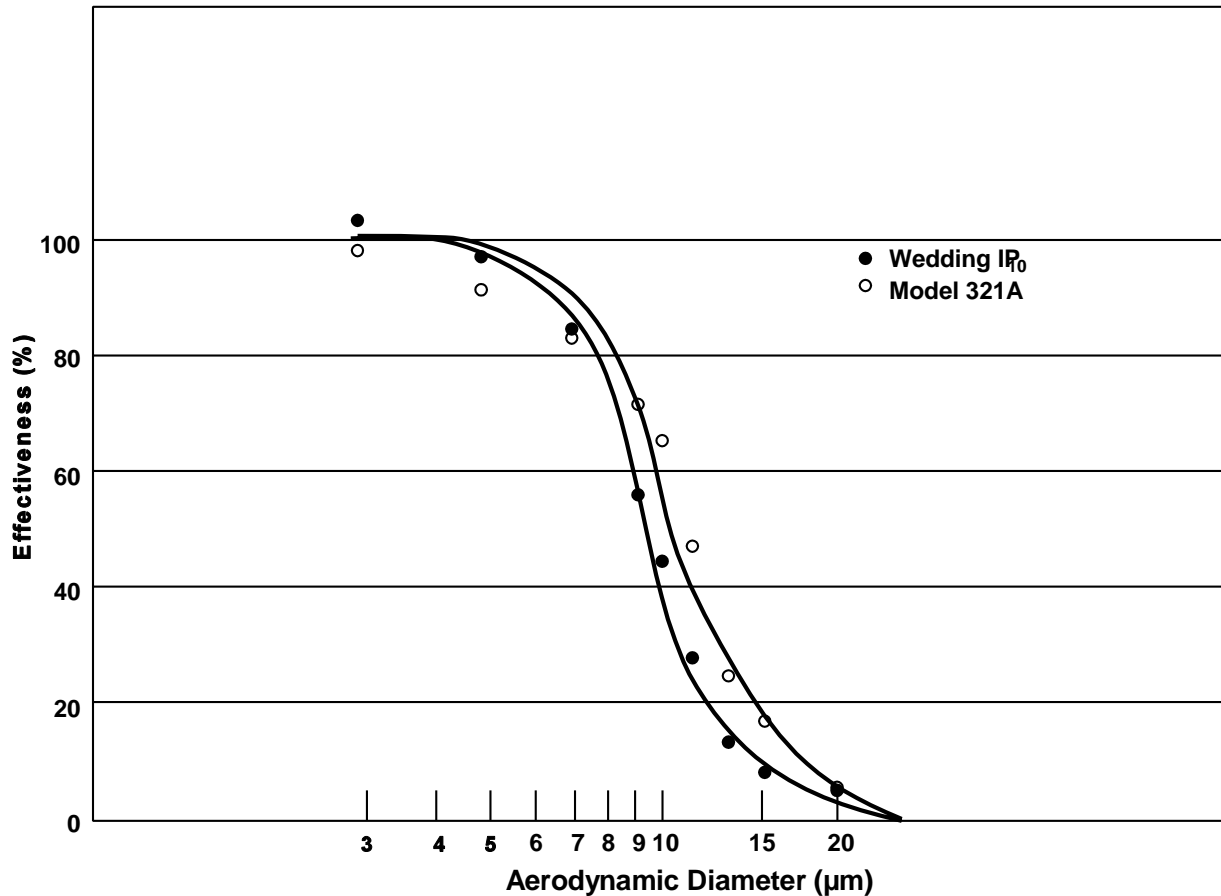
Marple and Rubow (1976) placed inertial impactors on the inlet of an optical particle counter to provide an aerodynamic calibration of the optical readout for non-ideal particles. Buettner (1990) noted that an aerodynamically calibrated optical particle counter could in turn be used to test the sampling performance of other devices only if the particle shape and refractive index of the test aerosol were consistent between calibrations. Maynard (1993) used this approach to determine the penetration of a respirable cyclone to polydisperse glass microspheres, using the TSI, Inc. Aerodynamic Particle Sizer (APS). John and Wall (1983) noted that inaccurate inlet sizing results may be obtained using poly-disperse AC test dust, as the result of agglomeration. Kenny and Lidén (1991) used the APS to characterize personal sampler inlets

and observed that, on theoretical grounds, calm air sampling would be expected to provide unity aspiration efficiencies for particles below about  $8\ \mu\text{m}$ . Tufto and Willeke (1982) used an optical particle counter (OPC) to monitor monodisperse aerosols in a wind tunnel setting to determine the performance of aerosol sampling inlets relative to an isokinetic nozzle. Yamada (1983) proposed using electron microscopy to determine the size distributions of polydispersed particles using manual counting techniques before and after a candidate aerosol separator. Penetration data from this technique were found to be significantly less precise and more difficult to interpret compared with data for the same separators using fluorometric methods.

The aerosol cutpoint performance of two  $\text{PM}_{10}$  samplers that have met the EPA performance specifications is illustrated (see Figure 4-4) by the data for the Andersen 321A and Wedding  $\text{IP}_{10}$  high volume sampler inlets at 8 km/h from Ranade et al. (1990). The data show that the cutpoint requirements, defined as a  $D_{50}$  of  $10.0\ \mu\text{m} \pm 0.5\ \mu\text{m}$  and mimicking a modeled cutpoint sharpness ( $\sigma_g$ ), were met for each of the tested wind speeds. These performance results were verified by repeating the tests in wind tunnels located at two other research facilities. A diagram (U.S. Environmental Protection Agency, 1992) of the two-stage Sierra-Andersen  $\text{PM}_{10}$  high volume sampler inlet with a design flowrate of  $1.13\ \text{m}^3/\text{min}$  is shown in Figure 4-5. The buffer chamber of this inlet serves to dampen the particle-laden air stream passing through two sets of acceleration nozzles, which deposit particles larger than  $\text{PM}_{10}$  on internal collection surfaces. The  $\text{PM}_{10}$  fraction is typically collected by a glass fiber filter. An oiled impaction shim was incorporated into the first stage fractionator of the 321A to minimize reentrainment of deposited particles during field sampling. This modified version (Sierra-Andersen 321B) was designated as an EPA reference method for  $\text{PM}_{10}$  in 1987. A subsequent single-stage fractionator (Sierra-Andersen 1200) was developed<sup>5</sup> and designated as an EPA reference method, with a  $D_{50}$  of  $9.5\ \mu\text{m}$  and a hinged design to facilitate cleaning and oiling of the oiled impaction shim.

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<sup>5</sup>Graseby-Andersen, Inc., Atlanta, GA.

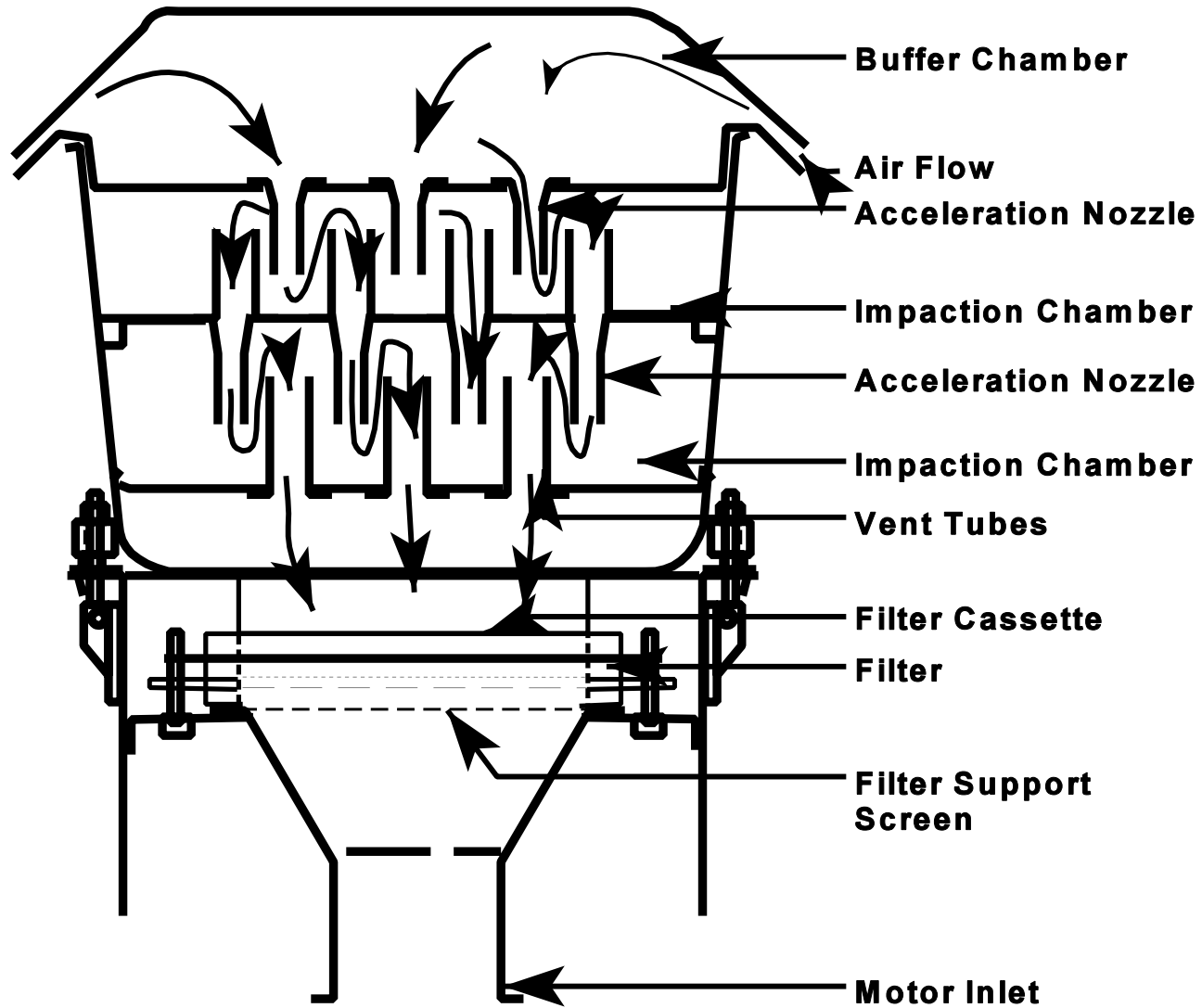


**Figure 4-4. Liquid particle sampling effectiveness curves with solid particle points superimposed for the Wedding IP<sub>10</sub> (•) and the Andersen Samplers Model 321A inlets at 8 km/h.**

Source: U.S. Environmental Protection Agency (1992).

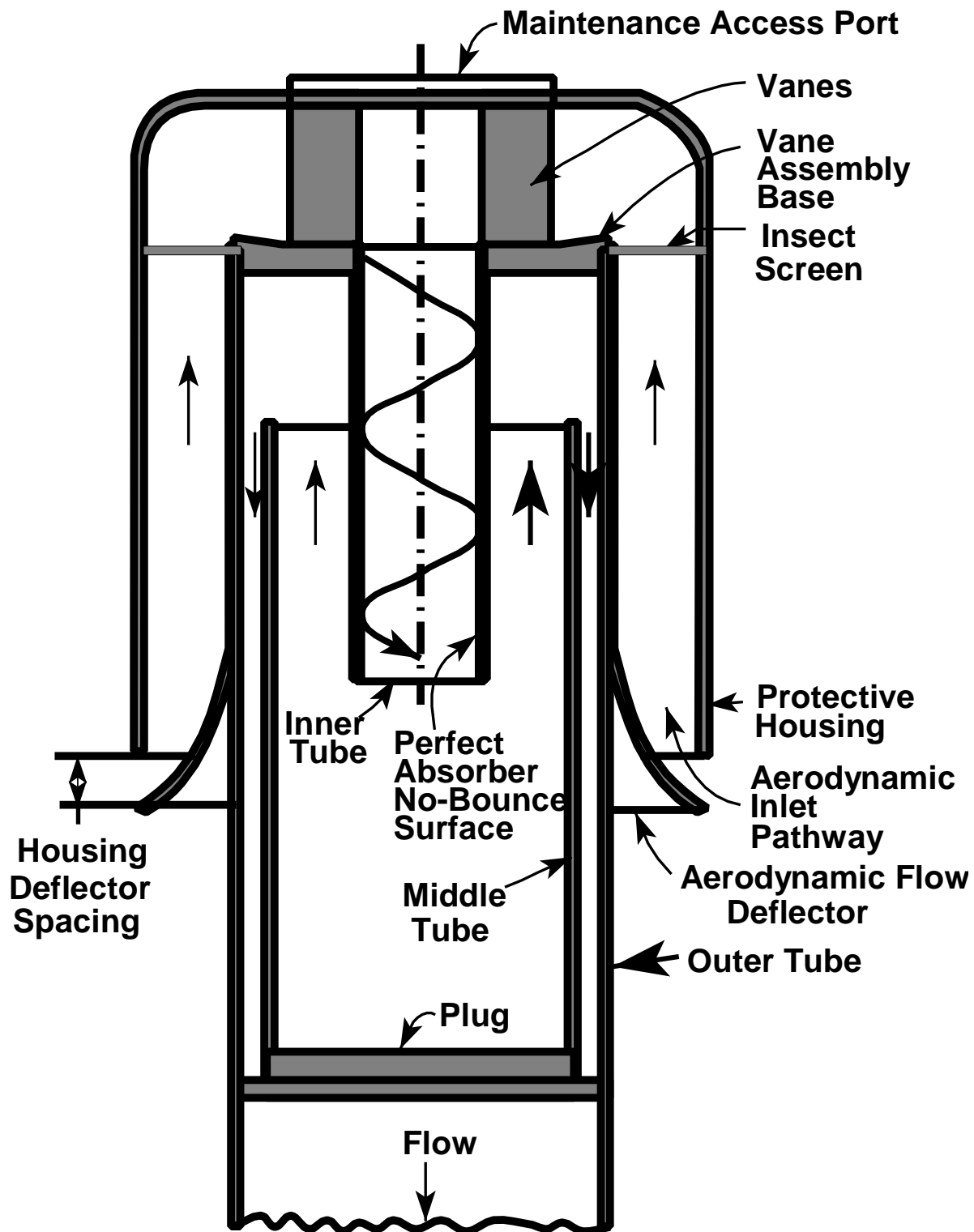
A diagram of the cyclone-based Wedding<sup>6</sup> PM<sub>10</sub> high volume sampler inlet (U.S. Environmental Protection Agency, 1990) with a design flowrate of 1.13 m<sup>3</sup>/min is shown in Figure 4-6. This inlet uses an omni-directional cyclone to accelerate the particle-laden air stream to deposit particles larger than PM<sub>10</sub> on an oiled collection surface. Two additional turns are made to alter the flow into a downward trajectory toward the collection filter. A brush is used to clean the deposited aerosol from the absorber surface through an access port. This inlet was designated as an EPA reference method for PM<sub>10</sub> in 1987.

<sup>6</sup>Wedding and Associates, Fort Collins, CO.



**Figure 4-5. Two-stage Sierra Andersen PM<sub>10</sub> sampler.**

Source: U.S. Environmental Protection Agency (1992).



**Figure 4-6. Sampling characteristics of two-stage size-selective inlet for liquid aerosols.**

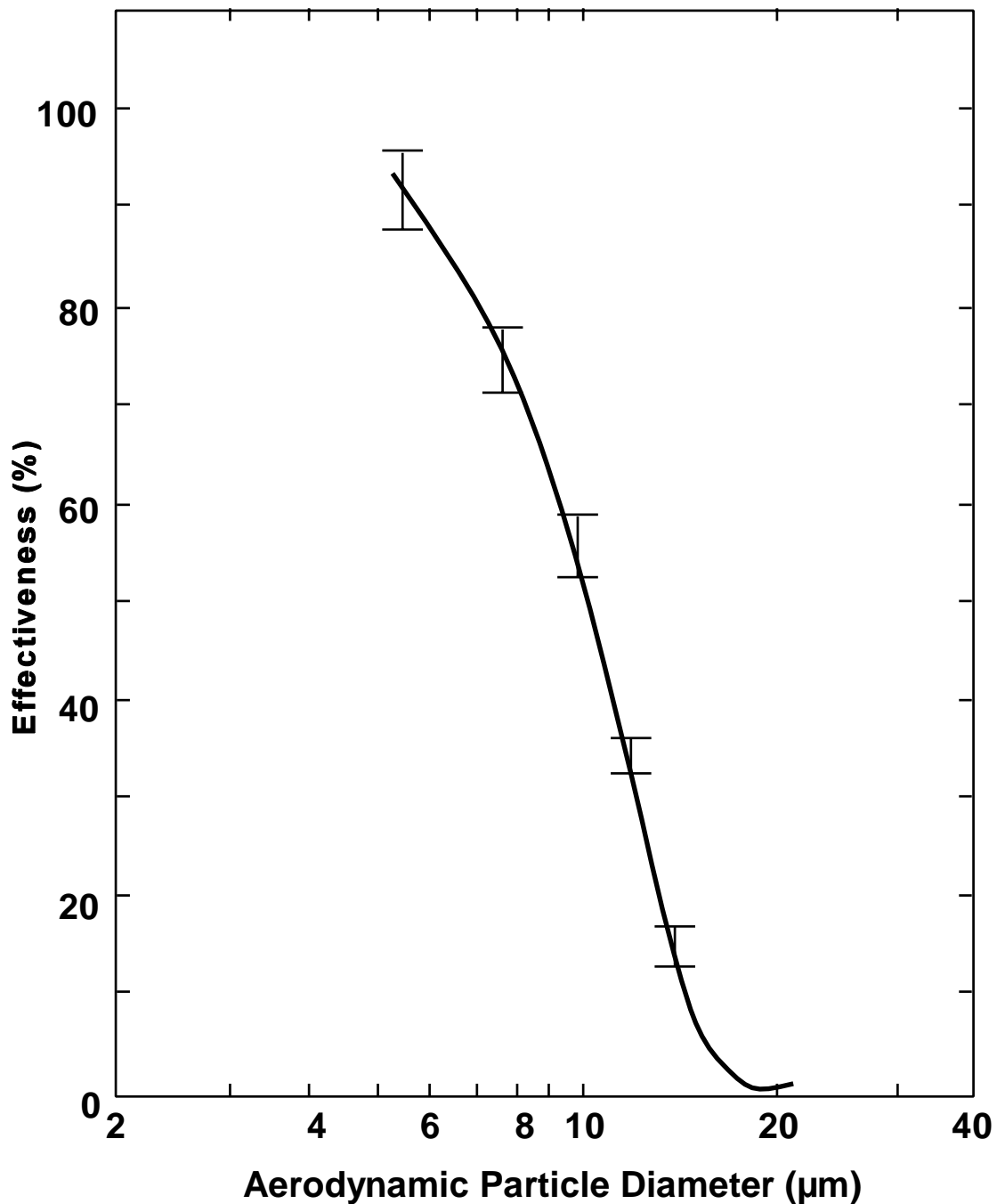
Source: U.S. Environmental Protection Agency (1992).



The aerosol collection performances for 16.67 lpm PM<sub>10</sub> inlets for the dichotomous sampler are described by Wedding et al. (1982) and McFarland and Ortiz (1984) and are illustrated by the penetration data in Figure 4-7. The variability of the performance as a function of wind speed for the Andersen 321A PM<sub>10</sub> inlet is shown in Figure 4-8 from data by McFarland et al. (1984). This is a dramatic improvement over the variability shown by the TSP high volume sampler (McFarland and Ortiz, 1979) for the same wind speed range. An attempt to simplify the complexity and improve the availability of wind tunnels to test PM<sub>10</sub> inlets was addressed by Teague et al. (1992), who describe a compact tunnel 6 m long by 1.2 m high that is capable of testing inlets against the EPA PM<sub>10</sub> specifications.

Watson and Chow (1993) noted that the EPA PM<sub>10</sub> performance specifications allowed a tolerance range around the D<sub>50</sub> that permitted inlets to be undesirably "fine tuned" to provide a cutpoint on the lower or upper end of the range. Since a significant amount of mass in the atmospheric aerosol may be associated with particles in the allowable tolerance range, a "reduction" in reported concentrations could be achieved by simply using a lower (e.g., 9.6 μm) cutpoint inlet that is still within the acceptable D<sub>50</sub> range. The biases between acceptable samplers have been apparent in the data from field aerosol comparison studies (e.g., Rodes et al., 1985; Purdue et al., 1986; Thanukos et al., 1992). Most of the reported biases between samplers were less than 10%, although some differences greater than 30% were reported. The data suggested that the collection efficiency of the high volume sampler PM<sub>10</sub> inlets based on cyclonic separation (Wedding, 1985) were consistently lower, while those based on low velocity impaction (McFarland et al., 1984) were consistently higher. Sweitzer (1985) reported results of a field comparison of these two high volume sampler types at an industrial location and reported average biases of 15%. It was noted that this amount of bias was unacceptable for compliance monitoring and more stringent performance requirements should be used. Rodes et al. (1985) observed that the PM<sub>10</sub> concentration data from the dichotomous sampler (regardless of the inlet design) gave the most predictable results.

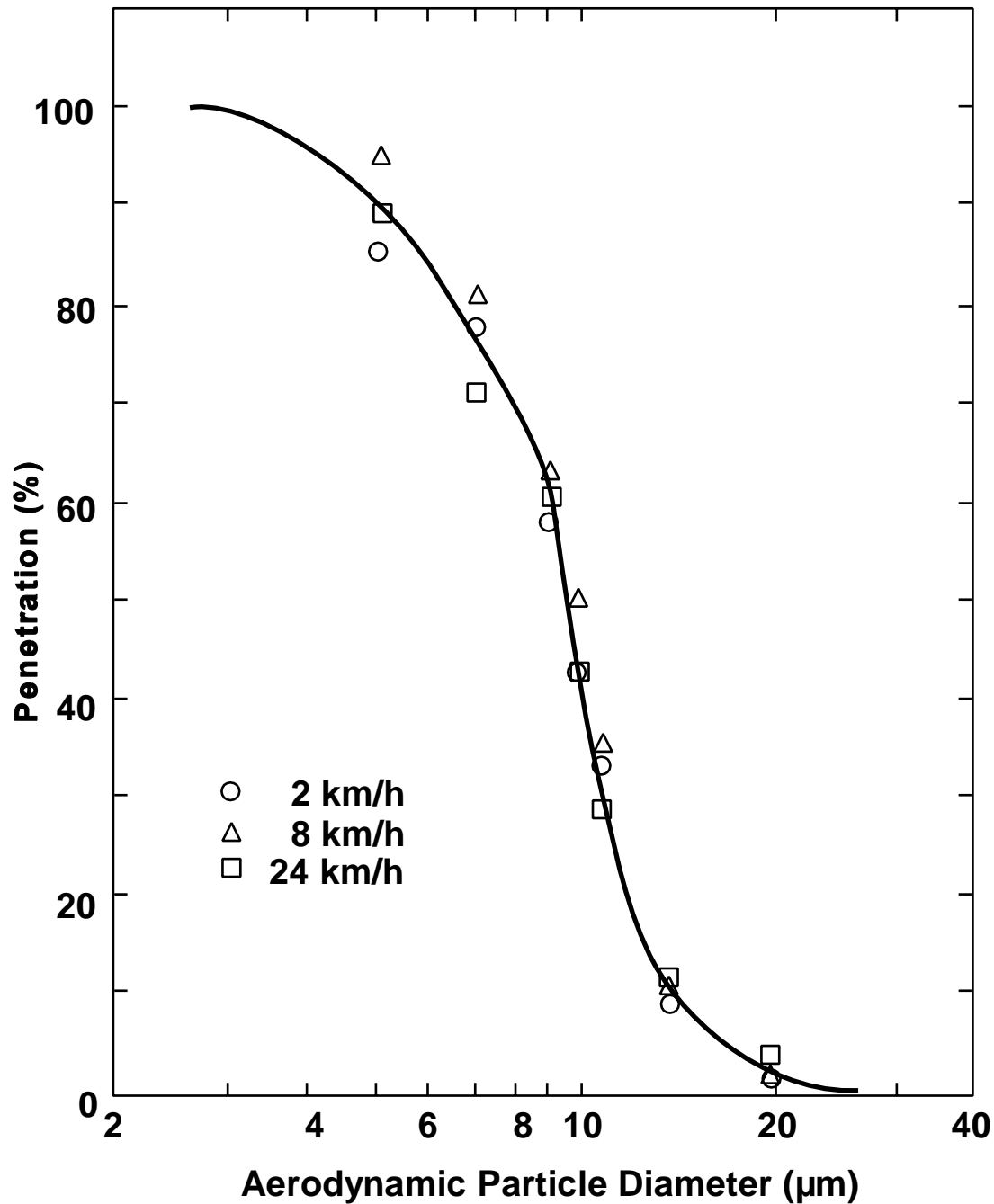
Wang and John (1988) were critical of the EPA PM<sub>10</sub> performance specification on allowable particle bounce (U.S. Environmental Protection Agency, 1987), stating that the criteria can lead to a 30% overestimation of mass under worst-case conditions. In a related paper, John et al. (1991) reported that although reentrainment by air flow alone of particles



**Figure 4-7. Penetration of particles for 16.67 lpm dichotomous sampler PM<sub>10</sub> inlets.**

Source: McFarland et al. (1984).

deposited in an aerosol inlet is typically negligible, reentrainment caused from subsequent particle deagglomeration caused by "bombardment" can be substantial. John and Wang (1991) suggested that particle loading on oiled deposition surfaces can bias the collection



**Figure 4-8. Collection performance variability illustrating the influence of wind speed for the Andersen 321A PM<sub>10</sub> inlet.**

Source: McFarland et al. (1984).

(2.2%/gram deposited) and strongly suggested that periodic cleaning and re-oiling should be required for PM<sub>10</sub> inlets. Özkaynak et al. (1993) observed that immediately after inlets of the

Wedding (1985) design were cleaned, an underestimation (compared to the dichotomous sampler) occurred of 14%. This bias was followed by a steady "recovery" period of 2 days, until the expected performance returned. They also observed a strong influence of diurnal temperature change on the ratios of concentrations between the Wedding (1985) design samplers and other PM<sub>10</sub> samplers. This influence could not be attributed to a physical phenomenon.

The EPA PM<sub>10</sub> performance specification program should be considered successful (John and Wall, 1983) in providing consistent aerosol collection results during field sampling. As noted by Thanukos et al. (1992), the cases of greatest concern were those where the measured concentrations were near an exceedance level. Wiener et al. (1994) noted that EPA was scrutinizing the current performance of designated reference and equivalent sampling methods for PM<sub>10</sub> in light of reassessment of the existing standard. A review of the current PM<sub>10</sub> performance requirements and possible amendments of the existing specifications may be appropriate, given the information base now available.

Laboratory and field testing reported in the literature since 1987 suggest that the EPA PM<sub>10</sub> Federal Reference Method (FRM) specifications and test requirements have not adequately controlled the differences observed in collocated ambient PM<sub>10</sub> sampling. The most significant performance flaws have combined to produce excessive (up to 60%) mass concentration biases. These biases apparently resulted from the combined factors of (1) allowing a cutpoint tolerance ( $10 \pm 0.5 \mu\text{m}$ ), (2) an inadequate restriction placed on internal particle bounce, and (3) a degradation of particle separation performance as certain technology PM<sub>10</sub> inlets became soiled. Particle bounce or soiling problems have not been reported for the PM<sub>10</sub> inlets for the dichotomous sampler.

A cutpoint tolerance of  $\pm 0.5 \mu\text{m}$  was required to account for expected differences between different wind tunnel laboratories testing the same hardware. The between-sampler bias from this tolerance limit alone is predictable and should provide PM<sub>10</sub> concentration differences significantly less than  $\pm 10\%$  in most cases. Particle bounce allowances are not as predictable, but design practices (primarily surface coatings with viscous oil, as suggested by John et al. [1991]) to minimize the penetration caused by bounce and resuspension have been shown to be very effective when properly serviced. The influences of internal surface soiling on PM<sub>10</sub> inlet performance were not recognized when the FRM was established in 1987, but were found to have severe consequences for some separation technologies. The magnitude of biases from

soiling is also not readily predicted, but can be ameliorated by not allowing the inlet to become excessively dirty during operation by routine cleaning prior to sampling.

Although the EPA test procedures have not been formally amended since 1987, the manufacturers of the designated  $PM_{10}$  reference methods (see section 4.2.6) have voluntarily modified their hardware designs and instruction procedures to accommodate particle bounce and soiling concerns. The SA-321b and SA-321c  $PM_{10}$  inlets were voluntarily withdrawn from the market by the vendor because of excessive biases attributed to particle bounce. The manufacturer now sells the SA1200 inlet which provides oiled surfaces to eliminate particle bounce and access screws to facilitate cleaning. The manufacturer also amended the instruction manuals to require a routine cleaning schedule. Similarly, the manufacturer for the Wedding  $PM_{10}$  inlet now provides an access port in the inlet and a cleaning procedure that can be applied prior to the collection of each sample. Based on our current understanding of the  $PM_{10}$  sampling process, it could be expected that sampling systems can be designed and concentration measurements made that are within 10% of the true concentrations.

## **4.2.3 Fine Particle Separators**

### **4.2.3.1 Cutpoint Considerations**

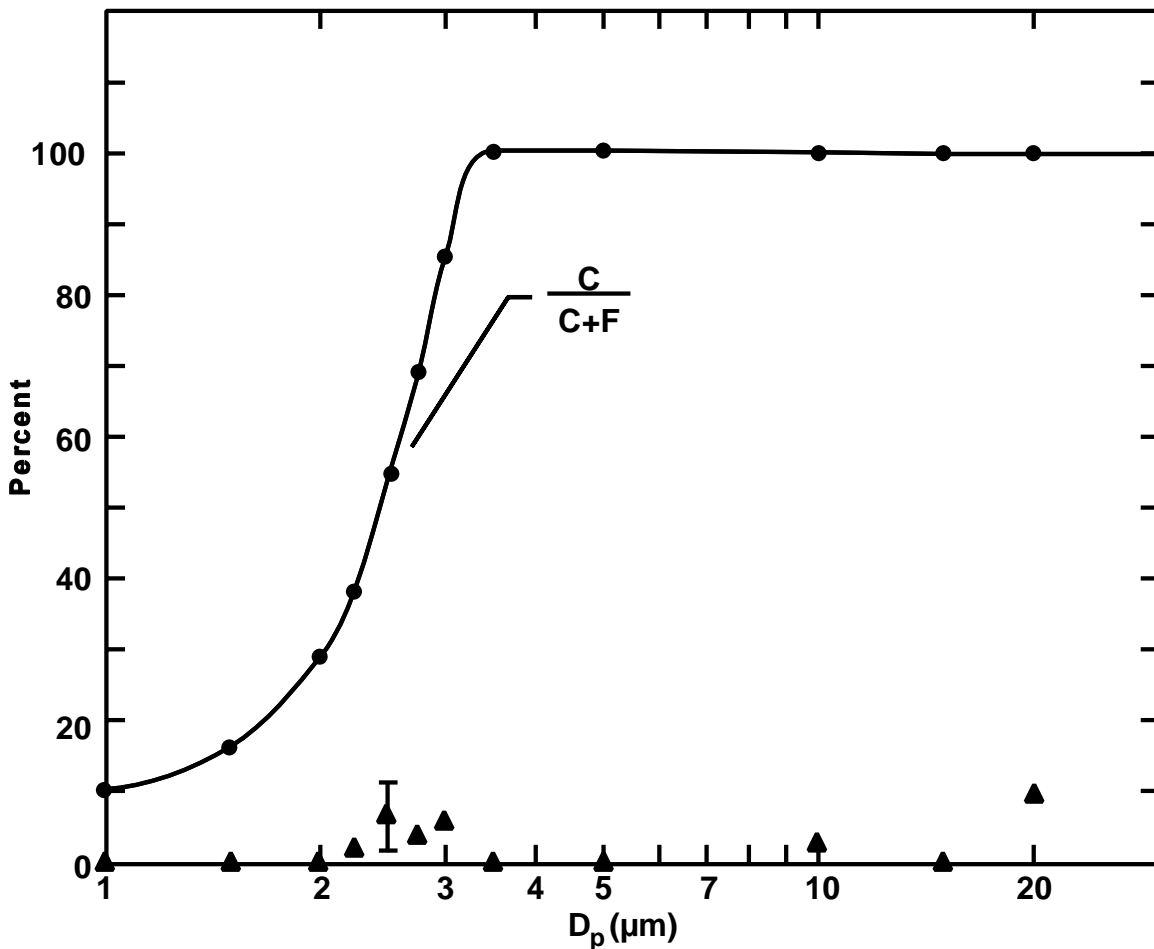
Although a particle separation at  $2.5\ \mu\text{m}$  has been utilized by the dichotomous sampler for a number of years, the 1987 standard reassessment (U.S. Environmental Protection Agency, 1987) did not specifically require routine monitoring for fine particles. It has become apparent (see Chapters 8 and 12) that certain health and ecological responses are most strongly correlated with fine particles, significantly smaller than  $10\ \mu\text{m}$ , and their related chemistry. Since the mass of a particle is proportional to the cube of its diameter, larger particles (especially above  $10\ \mu\text{m}$ ) can totally dominate the mass of  $PM_{10}$  and TSP samples. The  $2.5\ \mu\text{m}$  cutpoint generally occurs near a minimum in the mass distribution, minimizing mass concentration differences between samplers with cutpoint biases. The development of control strategies based on mass concentrations from a smaller cutpoint standard must be carefully constructed, especially if large particle interference problems (e.g., particle bounce) cannot be appropriately minimized.

Practical considerations would be the time and expense required to develop separators with  $1.0\ \mu\text{m}$  cutpoints that meet required specifications, conduct validation testing, and retrofit existing samplers. A virtual impaction "trichotomous" sample was described by Marple and

Olson (1995) that uses a  $PM_{10}$  inlet and separators for both 2.5 and 1.0  $\mu m$  cutpoints. They also noted that technology was not a limiting factor in providing a fine particle separator. Given the body of data available at 2.5  $\mu m$ , a focused effort may prove practical that defines the characteristics of the particle mass and chemistry between 1.0 and 2.5  $\mu m$ . This would add to the technical knowledge base, allow interpretive corrections between cutpoints to be made, and permit continued sampling at 2.5  $\mu m$  with a minimum of additional resources.

#### **4.2.3.2 Virtual Impactors**

The dichotomous sampler utilizes virtual impaction to separate the fine ( $<2.5 \mu m$ ) and coarse (2.5 to 10  $\mu m$ ) fractions into two separate flowstreams (see, for example, Novick and Alvarez, 1987) for collection on filters. The calibration of a nominal 2.5  $\mu m$  impactor, including wall loss data, is shown in Figure 4-9 (from Loo and Cork, 1988). The current separator design was shown to provide a relatively sharp cutpoint with minimal internal losses. A virtual impactor has been designed with a 1.0  $\mu m$  cutpoint (Marple et al., 1989), and for cutpoints as small as 0.12  $\mu m$  (Sioutas et al., 1994). After a cross-channel correction factor for the coarse mode is applied, the mass concentrations of each fraction and the total mass (using a  $PM_{10}$  inlet) can be determined gravimetrically. An inherent consideration with virtual separation is contamination of the coarse fraction by a portion of the fine fraction, equivalent to the ratio of the coarse channel flow to the total flow (typically 10%). Although a straightforward mathematical correction can account for the particle mass between channels, this can influence subsequent chemical and physical characterizations, if significant differences exist between the chemistry of each fraction (e.g., acidic fine fraction and basic coarse fraction). Stevens et al. (1993) utilized this limited addition of fine particles to the coarse fraction to advantage in the SEM analysis of samples collected on Nuclepore



**Figure 4-9. Aerosol separation and internal losses for a 2.5- $\mu\text{m}$  dichotomous sampler virtual impactor.**

Source: Loo and Cork (1988).

filters. Keeler et al. (1988) showed that the growth of fine aerosols at elevated relative humidities can significantly alter the ratio of fine to coarse collection for the dichotomous sampler. During early morning periods when the humidity approached 100%, an apparent loss of up to 60% of the fine mass (to the coarse channel) was observed. Keeler et al. (1988) concluded that analyzing only the fine fraction of the measured aerosol may not be appropriate, especially for short integration intervals.

A high volume ( $1.13 \text{ m}^3/\text{min}$ ) virtual impactor assembly was developed by Marple, et al. (1990) that can be placed on an existing high volume sampler to permit larger total collections than the dichotomous sampler for chemical speciation by size fraction. By placing a number of

virtual impactors in parallel, a separation can be achieved at higher flows, while reducing the total pressure drop. Marple et al. (1993) provide a list of commercially available virtual impactors by flowrate and available cutpoints. They also note that virtual separators inherently concentrate the particles in the coarse fraction (typically by a factor of 10), making them useful as pre-concentrators for sensors with marginal sensitivities. John et al. (1983) found that an oiled Nuclepore filter with a nominal 8  $\mu\text{m}$  porosity could provide a  $D_{50}$  cutpoint of 2.5  $\mu\text{m}$ , similar to that of a virtual impactor, if operated at the appropriate face velocity and for a sampling period short enough to minimize overloading.

#### 4.2.3.3 Cyclones

Cyclones have been used as aerosol separators in personal exposure sampling in occupational settings for many years. Lippmann and Chan (1979) summarized the cyclones for sampling aerosol sizes below 10  $\mu\text{m}$  and noted that the aerosol penetration through a cyclone can be designed to closely mimic respiratory deposition. An intercomparison of three cyclone-based personal exposure samplers under occupational conditions (concentrations typically > 1  $\text{mg}/\text{m}^3$ ) was described by Groves et al. (1994). They reported that even though the cyclones were reportedly designed to mimic similar respirable conventions, biases as large as a factor of two were noted, possibly attributable to overloading problems. Marple et al. (1993) provided a list of commercially available air sampling cyclones, by sampling flowrate and  $D_{50}$  range. Cyclones can be used individually or in a cascade arrangement to provide a size distribution. Bartley and Breuer (1982) describe methods to reduce biases when using a 10 mm (diameter) personal air sampling cyclone, especially as related to cutpoint shifts caused by flowrate changes. Saltzman (1984) provided a similar analysis for atmospheric sampling cyclones. Sass-Kortsak et al. (1993) observed that substantial uniformity-of-deposition problems can occur on the filters downstream of personal sampling cyclones. Wedding and Weigand (1983) used a cyclone within a high volume aerosol inlet to provide a  $\text{PM}_{6.0}$  cutpoint for ambient sampling that did not allow penetration of particles greater than 10.0  $\mu\text{m}$ .

The simplicity of cyclones has prompted their use as inlets and subsequent separators in samplers designed to fractionate the aerosol sample for chemical analysis. The "Enhanced Method" employed by EPA for sampling acidic aerosols uses a glass cyclone with a 2.5  $\mu\text{m}$  cutpoint as the sampler inlet (U.S. EPA, 1992). The percent collection as a function of

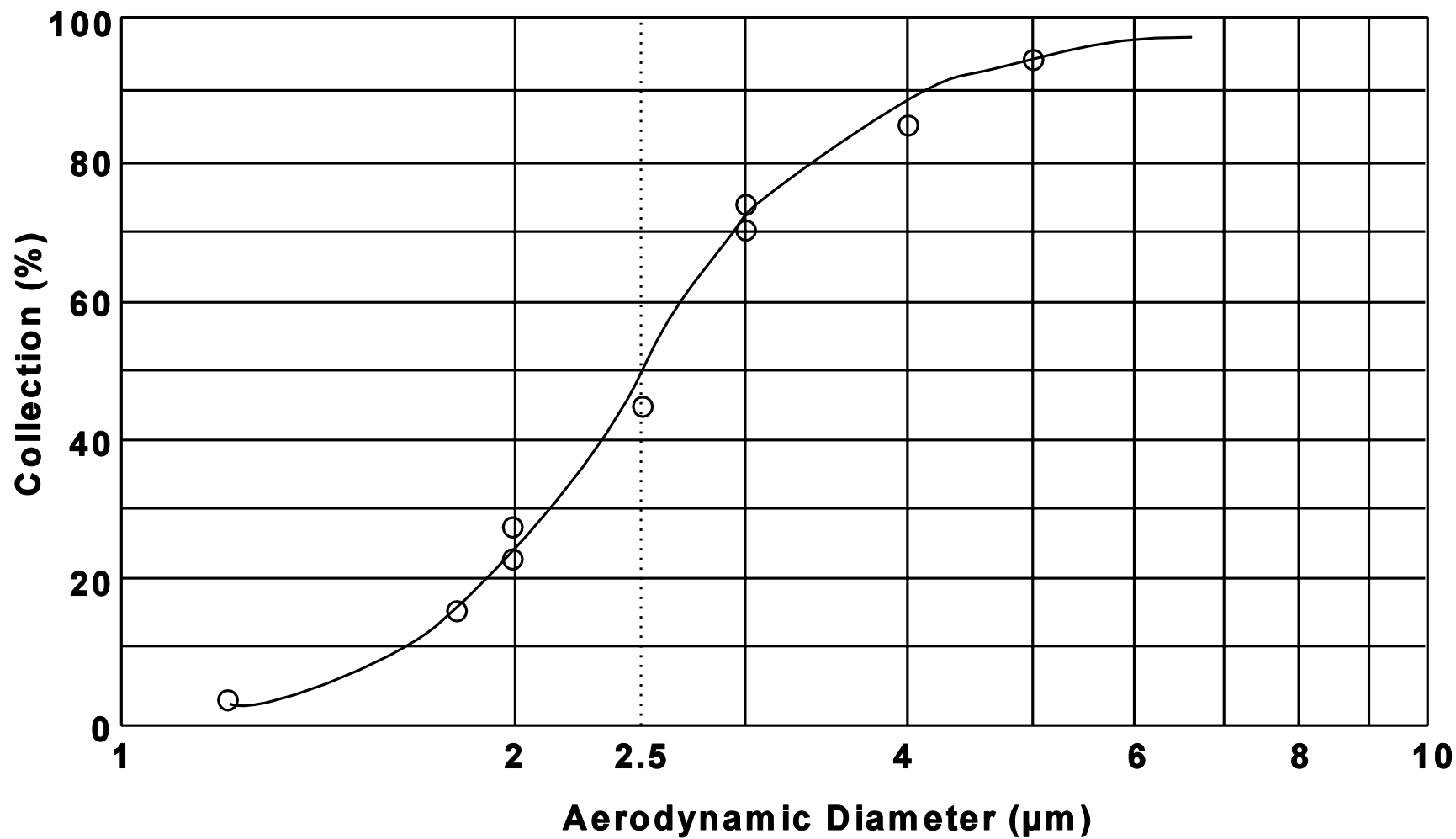


aerodynamic diameter is shown in Figure 4-10 (Winberry et al., 1993). The modest cutpoint sharpness exhibited by some cyclones should be considered when attempting to separate particle size fractions that may interact chemically. Hering et al. (1990) describe several validated aerosol systems for sampling carbonaceous particles that utilize cyclones with 2.5  $\mu\text{m}$  cutpoints to sample the fine fraction on either Teflon or quartz substrates. Spagnolo and Paoletti (1994) describe a dual cyclone ambient aerosol sampler with a 15  $\mu\text{m}$  inlet (described by Liu and Piu, 1981). This sampler was designed to collect a 20 to 15  $\mu\text{m}$  fraction, a 20 to 4.0  $\mu\text{m}$  fraction, and a 0 to 2.5  $\mu\text{m}$  fraction. Malm et al. (1994) describe a sampling system with a  $\text{PM}_{10}$  inlet and three parallel channels following a 2.5  $\mu\text{m}$  cutpoint cyclone that was used for the 40 site IMPROVE network. Over 120,000 fine particle filter substrates of Teflon®, nylon and quartz were collected for chemical analysis over a 6 year period.

#### **4.2.3.4 Impactors**

Impactors have been developed for a wide range of cutpoints and flowrates. In cascade arrangements (see Section 4.2.7.1.1) with a characterized inlet, impactors provide particle distribution information over a range of aerodynamic sizes. Impactors used as components of inlets or as in-line fractionators stop and retain the aerosol on a surface (e.g., oil-soaked, sintered metal or glass) that provides consistent performance (primarily minimal bounce) over the entire sampling interval. Recovery and analysis of the deposited particles in these situations are usually not considerations. Koutrakis et al. (1990) described the design of 2.1  $\mu\text{m}$  cutpoint impactor for a single stage annular denuder system that exhibited internal losses of less than 3%. Marple (1978) described the use of multiple nozzle impactors in a single stage to emulate selected respiratory penetration curves.

Marple et al. (1993) noted that the three primary limitations of impactors are particle bounce, overloading of collection stages and interstage losses. Particles can bounce from a stage after impaction if the surface forces are not adequate for their retention. Wang and John (1988) described the effects of surface loading and relative humidity on particle bounce and growth, and they noted that if less than 6% of the impact area was covered by deposited



**Figure 4-10. Percent collection as a function of aerodynamic diameter for the U.S. Environmental Protection Agency enhanced method glass cyclone.**

Source: Winberry et al. (1993).

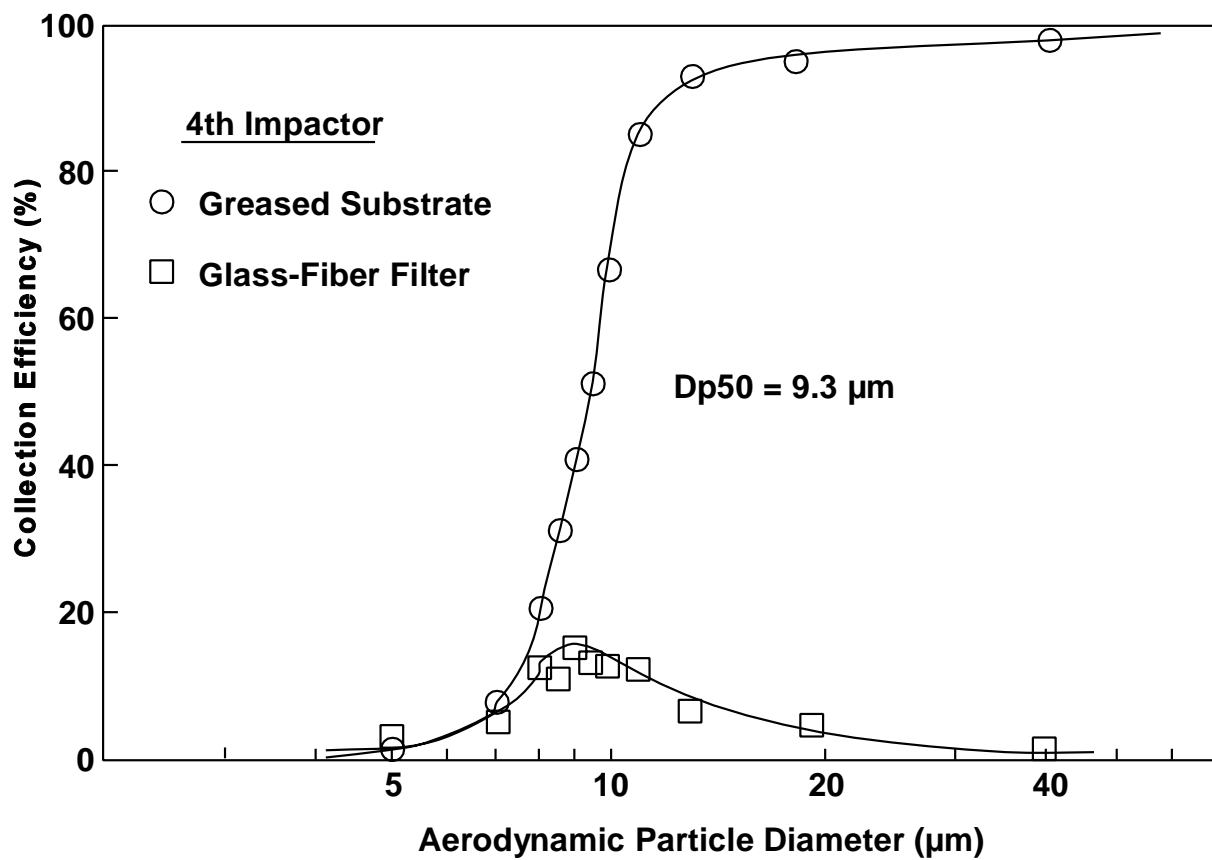
particles, particle-to-particle collisions (and bounce) could be neglected. They also showed that ammonium sulfate aerosol growth with increasing humidity resulted in a 25% shift in cutpoint as the relative humidity increased to 64%. Biswas et al. (1987) showed that, especially in low pressure zones, the relative humidity and temperature can change rapidly within a cascade impactor, potentially altering cutpoints and losses. Wang and John (1988) in subsequent work did not observe these shifts, noting that the transit time in a jet is only on the order of 10  $\mu$ s. Turner and Hering (1987) noted that the stage substrate materials (Mylar<sup>®</sup>, stainless steel and glass) with the same grease (Vaseline<sup>®</sup>) could produce substantially different particle adhesion characteristics. Vanderpool et al. (1987) showed that using glass fiber filters as impactor surfaces can produce drastically reduced performance as compared to a greased substrate (see Figure 4-11). Markowski (1987) suggested that adding a duplicate (same cutpoint) serial impactor stage can permit reasonable bounce and re-entrainment corrections to be made.

## **4.2.4 Sampling Considerations**

### **4.2.4.1 Siting Criteria**

Selection of aerosol sampling locations is partially guided by siting criteria under the 1987 PM<sub>10</sub> regulation (U.S. Environmental Protection Agency, 1987), which provided limited guidance for Pb and PM<sub>10</sub> samplers. The details behind these guidelines for PM<sub>10</sub> are provided in a guidance document (U.S. Environmental Protection Agency, 1987), which relates physical and chemical characteristics of aerosols to the spatial scales (regional, urban, neighborhood, middle and micro) required to define the influences of sources on various populations. Guidance was also provided on the influences of nearby point, line and area sources on sampling location as a general function of particle size. Only limited information was noted to be available on specific influences of local obstructions and topography (e.g., trees, buildings) on measured aerosol concentrations. The primary focus was establishment of the degree that a sampling location was representative of a specific scale.

The high purchase cost, and occasionally physical size, of aerosol samplers have restricted the number of sampling sites used in air monitoring studies. This may pose problems if the selected sites are not truly representative of the exposures for the populations at risk. To address the biases resulting from too few aerosol samplers in a field study, a



**Figure 4-11. Performance of glass fiber filters compared to greased substrate.**

Source: Vanderpool et al. (1987).

"saturation" sampler approach has been used, utilizing an inexpensive, miniature and battery-powered  $PM_{10}$  sampler that can be deployed at a large number of sites. Phillips et al. (1994) reported application of this approach, using 15  $PM_{10}$  saturation samplers in conjunction with one dichotomous sampler to study the contribution of diesel emissions to total PM levels in Philadelphia. Although the mean for  $PM_{10}$  concentrations of the saturation samplers was essentially identical to that of the dichotomous sampler, the saturation data showed site-to-site mean differences of up to  $30 \mu g/m^3$ .

#### **4.2.4.2 Averaging Time/Sampling Frequency**

The collection frequency for samples to support the EPA  $PM_{10}$  NAAQS has typically been on an every-6th-day schedule. Shaw et al. (1982) raised a statistically-based concern that

infrequent collection increases the coefficient of variation about the overall mean concentration value; that is, the variability of computed fine mass concentration means increased as the square root of the number of intervals between individual measurements. Symanski and Rappaport (1994), using time series analyses, described the influences of autocorrelation and non-stationary behavior in occupational settings on concentration distributions constructed from infrequent sampling. They recommended a random sampling design where a sufficient number of locations are sampled repeatedly over an adequate period of time to account for the full range of exposure possibilities. Hornung and Reed (1990) described a method of estimating non-detectable (or missing) values to lessen variance about the estimate of the geometric mean, by assuming that the concentration distribution is log-normal.

Insufficient sample collections can be remedied by more frequent operation of manual samplers. The recent  $PM_{10}$  equivalency designations (see section 4.2.5) of two beta gauge samplers and the TEOM sampler can provide the necessary information, with hourly rather than daily resolution. The initial cost of an automated sampler is typically 2-3 times that of a manual, single channel  $PM_{10}$  sampler, but can be offset by savings in operator labor costs. If inherent biases described in section 4.2.3.4 for the beta and TEOM samplers can be overcome (and they are field reliable), these approaches should prove very useful in routine regulatory and research monitoring studies. Potential also exists for the integrating nephelometer to be an acceptable exceedance monitor<sup>7</sup>, using site specific calibrations relating the measured scattering coefficient,  $b_{sp}$ , to fine aerosol mass concentrations (e.g., Larson et al., 1992).

Another consideration for defining sampling intervals is the setting of start and stop clock times. Daily 24-h sampling is most often done from midnight-to-midnight, but occasionally from noon-to-noon to either reduce the number of samplers required or to reduce operator burden. Sampling locations with highly variable diurnal aerosol concentration patterns (e.g., from night time wood smoke influence or day time traffic dust), or marked differences between week days and weekend days may require special consideration. These influences can be especially significant for <24-h sampling periods.

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<sup>7</sup>A Pollutant Standard Index (PSI) monitor used to estimate when a pre-determined exceedance level has been reached or exceeded, to potentially trigger the operation of an equivalent  $PM_{10}$  gravimetrically-based sampler.

#### 4.2.4.3 Collection Substrates

The selection of a filtration substrate for integrated collection of particles must be made with some knowledge of the expected particle characteristics and a pre-determined analytical protocol. The expected sampled size distribution places a requirement on the porosity of the filter media to effectively trap a reasonably high percentage of the particles with a minimum of pressure drop. The most common filter types used in air sampling are fiber and membrane. Fiber filters tend to be less expensive than membrane filters, have low pressure drops, and have high efficiencies for all particle sizes. They are most commonly available in glass fiber, Teflon coated glass fiber and quartz materials. Membrane filters retain the particles on the surface for non-depth analyses (e.g., X-Ray Fluorescence), can have specific porosity's, and are available in a wide variety of materials. Teflon is a popular membrane material because of its inertness, but is 2 to 4 times as expensive as more common materials. Liu et al. (1978) summarize the effective penetration characteristics as a function of particle size and pressure drops for a wide variety of fiber and membrane filters. The selection of filter diameter for a given flowrate influences the face velocity and the loading capacity before the pressure drop becomes unacceptable. A 47mm filter provides a surface area that is 60% larger than that of a 37mm filter. Polycarbonate filters with well defined porosities (e.g., Nuclepore®) have been used in "stacked" arrangements as fine particle separators. John et al. (1983) describe using an 8  $\mu\text{m}$  porosity filter in series with a back-up filter to effectively provide a 3.5  $\mu\text{m}$  separation of fine and coarse particles in a small, inexpensive package. Samplers based on this principle were widely used in the early 1980's (Cahill et al., 1990) and their performance under field conditions was shown to be equivalent to later cyclone based  $\text{PM}_{2.5}$  samplers in the IMPROVE network.

The reactivities of filter substrates with the aerosol have been reported extensively. A common problem with glass fiber filters used on high volume samplers is the basic pH of the glass material and its effective conversion of  $\text{SO}_2$  to particulate sulfates (e.g., Pierson et al., 1976). Appel et al. (1984) also reported similar conversions of nitrogen oxides to particulate nitrates on glass fiber filters. Witz et al. (1990) reported losses of particulate nitrates, chlorides and ammonium (19, 51 and 65%, respectively) from quartz fiber filters during storage. No significant losses of sulfates were reported from quartz filters. Similarly, Zhang and McMurry (1992) reported the anomalous loss of fine particle nitrates from Teflon filters and noted that predictive loss theories were insufficiently accurate to permit corrections. Lipfert (1994) also

observed that nitrate artifacts on glass fiber filters were difficult to quantify on a routine basis. Measurements of particulate nitrate using nylon filters by the IMPROVE protocols show, however, that such effects are minor except in California (Malm et al., 1994). Eatough et al. (1993) found significant losses of particulate organic compounds on quartz filters due to volatilization, such that ambient concentrations of particulate carbon may be underestimated substantially. Lipfert (1994) investigated filter artifacts in a field study in New York and concluded that positive sulfate artifacts inflated  $PM_{10}$  values from glass fiber filters by  $6 \mu\text{g}/\text{m}^3$ . It was noted that the combination of sulfate and nitrate artifacts on glass fiber filters may inflate TSP measurements by as much as 10 to  $20 \mu\text{g}/\text{m}^3$ .

#### **4.2.4.4 Chemical Speciation Sampling**

The collection of aerosol samples for chemical speciation analysis adds another dimension to the complexity of the sampling protocol (also see Section 4.3). The simplest approach utilizes a characterized inlet or separator to define a size fraction, provides an aerosol collection substrate compatible with the analytical technique, and collects an adequate quantity of sample for analysis. This approach is applicable for relatively nonreactive and stable components such as heavy metals. An important consideration is the potential reactivity of the sampling substrate with either the collected aerosols or the gas phase. Appel et al. (1984) predicted effects of filter alkalinity on conversion of acid gases to sulfates and nitrates and provided an upper limit estimate for artifact sulfate formation (added mass) for TSP high volume sampling of 8-15  $\mu\text{g}/\text{m}^3$  for a 24-h sample.

Analyses for semi-volatile organics found in both the particle and vapor phases must be collected by adding a vapor trap (e.g., polyurethane foam plug) downstream of the sampling filter. Arey et al. (1987) noted that this arrangement of sequential sampling reservoirs may account for the total mass of organics, but not accurately describe their phase distribution in situ, due to "blow-off" from the filter during sampling. Van Vaeck et al. (1984) measured the volatilization "blow-off" losses of organic species from cascade impactor sampling to be up to 30%, while the loss of total mass was only 10%. McDow and Huntzicker (1990) characterized the face velocity dependence for organic carbon sampling and provided correction models, based on adsorption losses to a backup filter. Turpin et al. (1994) examined organic aerosol sampling artifacts and highlighted the distinction between "organic carbon" and individual organic species.

They observed that organic carbon sampled from the atmosphere is unlikely to attain equilibrium between that in the gas phase and that adsorbed on a quartz fiber back-up filter. They also noted that under typical sampling conditions, adsorption is the dominant artifact in the sampling of particulate organic carbon, and longer sampling periods reduce the percentage of collected material that is adsorbed vapor. It was recommended that collection of aerosols for carbon analyses be made on a pre-fired quartz filter, with estimates of the adsorption artifact made from a quartz filter placed behind a Teflon filter in a parallel sampler.

For more highly reactive and unstable species, the recognition of the in situ character of the aerosol in the air must be identified and preserved during all facets of the sampling process to provide a representative and accurate sample. Durham et al. (1978) described a denuder to remove sulfur dioxide while sampling for sub-micron aerosols. Spicer and Schumacher (1979) observed that many artifact reactions may occur if stripping of nitric acid, sulfuric acid and ammonia is not performed during speciated aerosol sampling. Appel et al. (1988a) described the various loss mechanisms that apply to the aerosol and vapor phases while sampling for nitric acid. They noted that residence time, surface material compositions, and conditioning prior to sampling were the predominant variables affecting transmission efficiency.

The determination of strong acidity for atmospheric aerosols (U.S. Environmental Protection Agency, 1992) describes an "enhanced" method that recognizes the inter-relationships between the vapor and aerosol phases for each constituent and the potential interferences. An inlet cyclone or impactor is used to provide a  $2.5\ \mu\text{m}$  cutpoint to exclude the higher pH aerosols found in the coarse fraction of  $\text{PM}_{10}$ . As shown in Figure 4-12, denuders are used in the flowstream which selectively remove gas phase components with minimal, characterized losses of aerosol. Ye et al. (1991) determined the aerosol losses through an 10 lpm annular denuder system as a function of particle size. They noted that total particle losses were less than a few percent whether the denuders were coated or uncoated. Also, using parallel annular denuders, Forrest et al. (1982) found aerosol losses of only 0.2 to 2.2% for 0.3 to  $0.6\ \mu\text{m}$  particles and 4 to 5% for 1 to  $2\ \mu\text{m}$  particles.



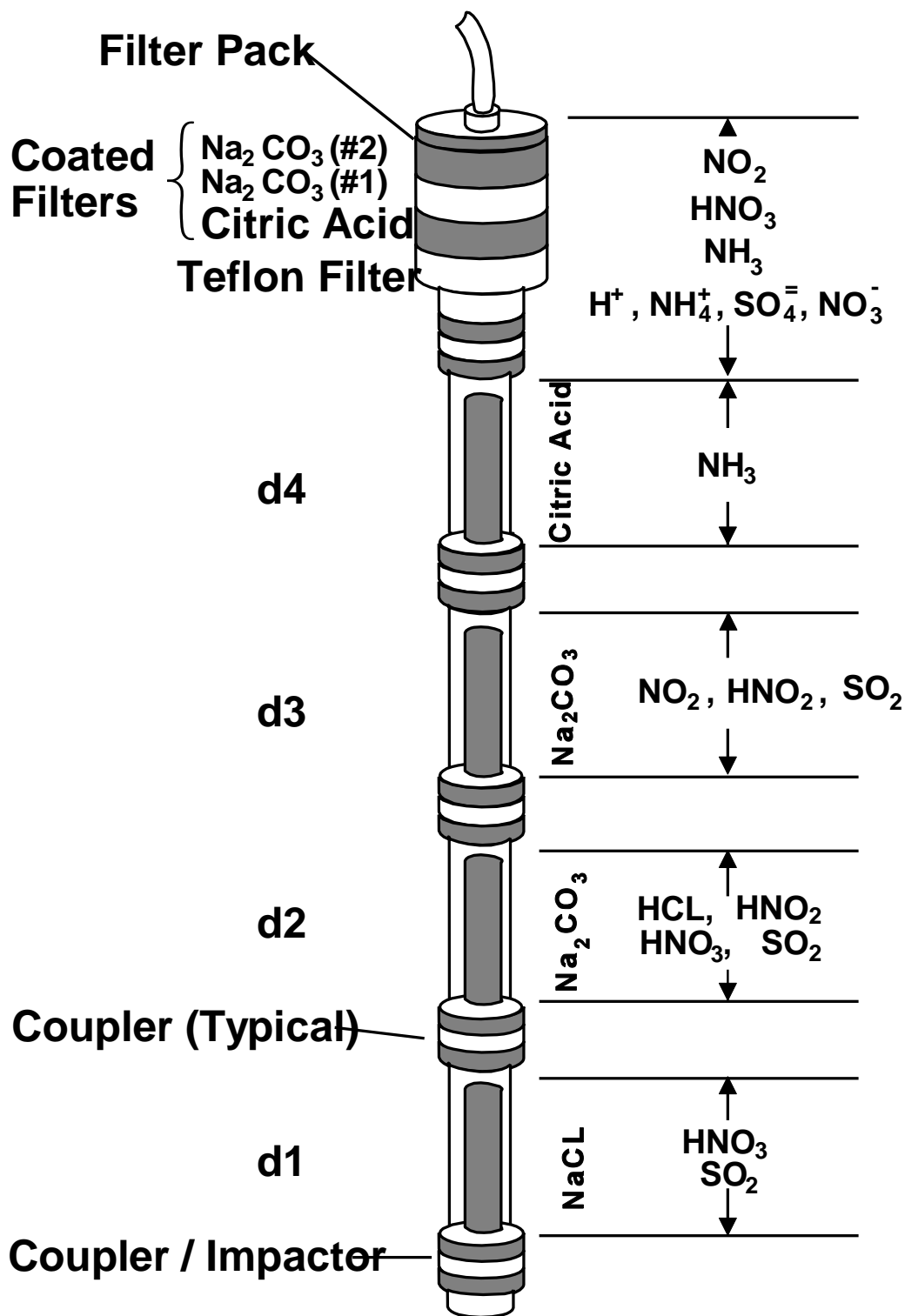


Figure 4-12. Schematic diagram of an annular denuder system.

Source: U.S. Environmental Protection Agency (1992).

Filter packs have been developed, consisting of a sandwich of filters and collection media of various types in series, to collect aerosols and selectively trap gases and aerosol volatilization products. Benner et al. (1991) described an annular denuder sampling system using Teflon and nylon filter packs and annular denuders to quantitatively collect the distributed ammonium nitrate, nitric acid and ammonia in the vapor and aerosol species. They observed that volatile nitrates were  $71\% \pm 27\%$  of the total nitrates during the day and  $55\% \pm 30\%$  at night in arid, southwestern U. S. locations. Masia et al. (1994) described the anomalous uptake of ammonia on the nylon filters, which were expected to collect only the gas phase nitric acid. Wang and John (1988) reported volatilization losses of ammonium nitrate in the Berner impactor of 7% under hot, dry (18% Rh) conditions.

Vossler et al. (1988) reported the results of improvements in an annular denuder system, including Teflon coating of the internal glass surfaces. They found an apparent particle bounce problem with the cyclone inlets (with or without Teflon coating) and proposed adding an additional in-line, greased impactor. John et al. (1988) found that anodized aluminum surfaces absorb nitric acid efficiently and irreversibly. Several method comparison studies have been reported for systems utilizing annular denuder/filter pack technologies, including Harrison and Kitto (1990), Sickles et al. (1990), and Benner et al. (1991).

#### **4.2.4.5 Data Corrections/Analyses**

Aerosol concentration data are reported in units of mass per volume (e.g.,  $\mu\text{g}/\text{m}^3$ ). The current EPA regulations for sampling TSP,  $\text{PM}_{10}$  and Pb require that sampler flowrates be controlled and the sampled volumes be standardized to 760 mm Hg and 25 °C. These requirements may pose problems in the interpretation of concentrations from aerosol samplers. Wedding (1985) notes that the flowrate through inertial impactors should be maintained at "local" temperatures and pressures to retain the separator's aerodynamic calibration. Mass flow controllers may significantly affect the separator flow velocity during large diurnal temperature changes, excessively biasing the resulting cutpoint diameter.

Subsequent correction of the sampled aerosol volume to "standard" conditions by mathematically compensating for average meteorological conditions may improperly report the aerosol concentration measurement. If the rationale for aerosol sampling was to mimic respiratory penetration (which occurred at local conditions), a correction after-the-fact may not

be appropriate. These corrections are typically small (less than a few percent) except in locations at higher altitudes and those with large diurnal or seasonal temperature changes. The basis for mandating flowrate controller performance for aerosol samplers is sound, but the subsequent requirements for concentration corrections for temperature and pressure are complex. Although the issue of sampled volume correction for local temperature and pressure is beyond the scope of this document, the scientific bases should be reassessed for aerosol sampling to determine if this requirement is consistent with EPA goals.

The matching of aerosol measurement capabilities with data quality requirements is discussed by Baron and Willike (1993). They note that although aerosol sampler precision can be determined from collocated measurements, field sampling accuracy is more difficult to define. Generation of mono- or polydisperse calibration aerosols are rarely done in field settings because of the complexity of the calibration process. Typically, only the aerosol sampler flowrate accuracy is determined in the field. Biases between the means from collocated aerosol samplers using different separation techniques, may result from sampler operational errors, or from inadequacies in determining the performance specifications during laboratory testing.

## **4.2.5 Performance Specifications**

### **4.2.5.1 Approaches**

A significant step in the standardization process for aerosol sampling was the EPA definition (U.S. Environmental Protection Agency, 1987) of the  $PM_{10}$  size fraction, based on the aerodynamic diameter of particles capable of penetrating to the thoracic region of the respiratory system. This definition was followed by implementation of the  $PM_{10}$  provisions of EPA's Ambient Air Monitoring Reference and Equivalent Methods regulation (U.S. Environmental Protection Agency, 1987). The format of the latter regulation included adoption of performance specifications for aerosol samplers, based on controlled wind tunnel testing with mono-dispersed aerosols. Controlled laboratory testing is followed by limited field testing, including tests of candidate equivalent methods to demonstrate comparability to designated reference methods. The stringency of the field testing to elucidate potential sampling biases is strongly influenced by the local sampling site environment, including factors such as wind speed, nearby point sources, and the probability of fugitive dust events.

This approach was chosen, rather than the design specification approach taken in 1971 (Federal Register, 1971), which identified the high volume sampler and associated operational procedures as the reference method for Total Suspended Particulates (TSP). The 1971 regulation had no provisions for the use of alternative or equivalent methods, and subsequent to this design designation, significant problems of the TSP high volume sampler, such as wind speed and direction dependency (McFarland et al., 1979) and off-mode collection (Sides and Saiger, 1976), were reported. These inherent biases complicated the interpretation of TSP concentration data (U.S. Environmental Protection Agency, 1982) and weakened correlations with other measures. The problems were estimated to have induced biases of less than 10% for most situations, but occasionally as high as 30%. The subsequent development of aerosol testing programs for size selective aerosol samplers (e.g., McFarland and Ortiz, 1979; Wedding, 1980; John and Wall, 1983; Ranade et al., 1990; Hall et al., 1992) more rapidly identified weaknesses in existing technologies and facilitated the development of better methods.

No reference standard exists for aerosol concentration measurements in air. The calibration of aerosol samplers relies primarily on characterizations under controlled conditions of the sampler sub-systems, including the size selective inlet, sample conditioning and transmission system, the flow control system, and, if used, subsequent size separators, sample collection and storage elements, and sensors and associated electronics. Although the precision of an aerosol sampler is readily obtained by using replicate, collocated samplers, the accuracy can only be estimated by comparison with either designated "reference" samplers or with computations of expected aerosol mass collections. Performance specification limits are used to control the overall aerosol sampling accuracy. As noted by John and Wall (1983) the selection of a comprehensive list of sampling elements requiring inclusion and the setting of the performance limits for each element is a difficult task, especially when the range of "real-world" sampling situations is considered.

Performance specifications were utilized for the  $PM_{10}$  standard to allow the broadest spectrum of measurement technologies, hopefully encouraging the development of new and better methods. A research program was implemented by EPA in parallel with preparation and review of the 1982 Criteria Document to identify the critical specifications and understand the inter-relationships among the parameters influencing the aerosol sampling process. Studies of the influences of factors such as wind velocity, particle character, flow rate stability, particle

bounce and wall losses on precision and accuracy substantially advanced the science of large particle sampling. The performance specification approach was a significant improvement over the design specification approach used for the TSP high volume sampler, in that it fostered the development of new information and technologies and provided for the use of alternative methods. In retrospect, the primary weakness of the design specification approach for the TSP reference method was not the process per se, but the technical inadequacy of the development and testing program that produced the high volume sampler design.

The utilization of a performance specification approach requires that a minimum level of knowledge be available about the measurement process and the associated test procedures. Some significant drawbacks subsequently observed in the performance specification approach for  $PM_{10}$  included the complexity, expense and scarcity of aerosol wind tunnel test facilities, and the difficulty in defining comprehensive specifications that considered all of the nuances of aerosol sampling. Wind tunnel evaluation and limited field tests do not always identify sampler related problems encountered during extended periods of ambient sampling (e.g., John and Wang, 1991). Future performance tests should ideally include extended field testing, for example, to evaluate performance in different geographic regions and seasons, as well as under different meteorological conditions.

#### **4.2.5.2 Performance Testing**

Since the 1982 Criteria Document (U.S. Environmental Protection Agency, 1982a), aerosol sampling research studies have identified numerous factors that influence the precision and accuracy of samplers in both wind tunnel and field performance testing. Rodes et al. (1985), Purdue et al. (1986), and Cook et al. (1995) showed, in field evaluations under a variety of sampling situations, that  $PM_{10}$  samplers meeting the EPA performance specifications provide aerosol concentration measurements with a precision of 10% or less when samplers of the same model were compared. However, significant biases were evident when different types of samplers were compared. The Andersen SA-321A  $PM_{10}$  sampler was found to collect an average of 58% more mass than a collocated Wedding  $PM_{10}$  sampler (Purdue et al., 1986). This was partly attributed to the (predicted) bias associated with cutpoint differences between the inlets. A more significant bias (not predicted) was associated with degraded performances in opposite directions (Andersen over-sampling, Wedding under-sampling) due to soiling of the

separators during extended sampling periods. Rodes et al. (1985) noted that sampler precisions (coefficients of variation) were better than  $\pm 10\%$ , with several samplers better than  $\pm 5\%$ . Cook et al. (1995) reported good agreement (variability less than 15%) among several types of  $PM_{2.5}$  samplers. Other sampler types showed significant biases. Under the conditions of the study, high concentrations of  $NH_4NO_3$  and organic carbon (winter in Bakerfield, CA), samplers which heated the collected particles to 30 °C or 50 °C during sampling gave lower mass values than filter samples which were collected at ambient conditions and equilibrated for 24 hours at  $23 \pm 3$  °C and  $40 \pm 5\%$  relative humidity. Coefficient of Haze (COH) measurements by an American Iron and Steel (AISI) tape sampler and light scattering ( $b_{scat}$ ) measured by an integrating nephelometer heated to 17 °C correlate well with  $PM_{2.5}$  measurements (COH,  $r = 0.82$  to  $0.91$ ;  $b_{scat}$ ,  $r = 0.91$  to  $0.98$ ).

Mark et al. (1992) reviewed the attributes of wind tunnel testing, and noted that tests using controlled conditions are a necessity to determine whether an aerosol sampler meets a basic set of established performance specifications. Hollander (1990) suggested that sampler performance criteria should be evaluated in controlled outdoor tests, given the inability of wind tunnels to accurately mimic the influences of outdoor meteorological conditions on sampling. The current EPA  $PM_{10}$  performance testing requires field tests to demonstrate sampler precision and flow rate stability, and the comparability of equivalent methods to designated reference methods. The stringency of such tests are highly dependent on the sampling location chosen, local aerosol sources, the existing meteorology and the season.

Kenny and Lidén (1991) noted that the EPA  $PM_{10}$  sampler performance specifications (U.S. Environmental Protection Agency, 1987) provided inadequate consideration for defining the uncertainty in each parameter, and they suggested that bias mapping approaches be considered. Bias mapping relates the allowable precision of a parameter to the critical values of expected bias that just meet the specifications. A similar but less robust procedure is used in the EPA performance specifications. Botham et al. (1991) recommended that the wind tunnel test system duplicate the expected field sampling scenarios as closely as possible, including characteristic flow obstructions. They described the wind tunnel testing of personal aerosol samplers mounted on an anthropogenically consistent (e.g., breathing, heated) mannequin. Hoffman et al. (1988) and John et al. (1991) described the adverse influence of internal surface soiling on aerosol collection performance during extended field operation, and noted that the

existing EPA PM<sub>10</sub> performance specifications only considered clean samplers. Mark et al. (1992) noted that even though wind tunnel performance testing cannot exactly emulate outdoor turbulence scales, testing in the controlled tunnel environment is a necessity to adequately characterize particle samplers.

Significant new innovations in aerosol sensing technologies that meet the PM<sub>10</sub> performance specification and have earned designations as equivalent methods (see Section 4.2.6) have occurred since the 1982 Criteria Document. These indirect<sup>8</sup> methods include automated beta attenuation monitors (e.g., Merrifield, 1989; Wedding and Weigand, 1993), and the automated Tapered Element Oscillating Microbalance (TEOM®) technology (Patashnick and Rupprecht, 1991). The TEOM® sampler does not use gravimetric analysis on a balance, but computes mass based on the frequency shift as particles are deposited on an oscillating element. These designations added automated sampling capabilities to the previously all-manual list of sampling methods. Recent field tests of both the beta and TEOM methodologies suggest that biases compared to gravimetrically-based samplers may exist that were not identified by the EPA performance test requirements. Arnold et al. (1992) provide data suggesting that the mass concentration data from a Wedding beta gauge averaged 19% lower than a collocated Wedding PM<sub>10</sub> gravimetric sampler. Several researchers reported that the TEOM can yield mass concentrations that are either lower or higher than those observed in reference method measurements (Hering, et al., 1994; Meyer, et al., 1992; Meyer et al., 1995). The TEOM operates at an elevated temperature (30 °C or 50 °C) during the collection and measurement process in order to ensure the removal of liquid water associated with particles. In the reference method, the particle-associated water is removed during an equilibration period in a specified temperature and relative humidity range. Both techniques are subject to loss of semivolatile materials such as NH<sub>4</sub>NO<sub>3</sub> and some organic components. The TEOM may lose semivolatile material that is volatilized due to the higher than ambient sampling temperatures. The reference method may lose semivolatile material during sampling (if concentrations decrease or temperature increases during the sampling period). The reference method is also subject to loss of semivolatile materials during equilibration and storage prior to weighing. These processes, in areas or times during which semivolatile aerosol components are a significant component of the

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<sup>8</sup>An alternate technology used instead of direct gravimetric analysis to infer mass concentrations from developed relationships.

ambient aerosol mass, can cause either technique to yield a significant under-estimation of the mass of particulate matter in the ambient air. This also applies to some degree to any integrated sample collected on a substrate. Devising comprehensive performance specifications and test procedures for aerosol samplers, given the complexities of aerosol chemistry, physics, and mechanics, is a demanding task.

The size-selective, gravimetrically-based, 24-h manual aerosol concentration measurement has been the mainstay of compliance sampling for at least two decades. Although several new sensor technologies have been designated as Equivalent methods for  $PM_{10}$  by EPA, no superior technology has been developed that is a better reference method than that based on collection of a discreet aerosol sample followed by gravimetric analysis. Improvements have been made since 1982 in the accuracy and precision of integrated, manual aerosol sampling. Some of the most significant advances have occurred in aerosol size separation technologies, improved performance characterization test methods, and speciation sampling techniques.

As discussed by Lippmann (1993), there may be no threshold for health responses down to the lowest aerosol concentrations. This implies that the precision and lower detection limit requirements will continue to be important for aerosol measurements across the concentration spectrum. These factors become even more critical as the size fraction of interest becomes smaller and fewer total particles are collected. At low concentrations (especially with small size fractions), normally insignificant factors can become important contributors to biases. Witz et al. (1990) reported rapid and substantial losses of nitrates, chlorides and ammonium ion (19, 65 and 51%, respectively) from quartz high volume sampler filters during storage periods of one week prior to analyses. Transformations can also occur on glass fiber substrates during sampling, as reported by Sickles and Hodson (1989) for the rapid conversion of collected nitrites to nitrates in the presence of ozone. Zhang and McMurry (1992) showed that nearly complete evaporative losses of Fine particle nitrate can occur during sampling on Teflon filters. Lioy et al. (1988), in a study using  $PM_{10}$  samplers, reported 25 to 34% lower concentration values resulting from losses of glass fibers from the filter to the filter holder gasket during sampling. Feeney et al. (1984) reported weight gains in Teflon filters used in contaminated ring cassettes, that posed significant problems for light aerosol loadings. Grinshpun et al. (1993) suggest that if unavoidable changes in the aerosol occur during sampling, development of a model that permits back-calculation of the in situ characteristics can be considered.



#### 4.2.6 Reference and Equivalent Method Program

Ambient air  $PM_{10}$  measurements are used (among other purposes) to determine whether defined geographical areas are in attainment or non-attainment with the National Ambient Air Quality Standards (NAAQS) for  $PM_{10}$ . These measurements are obtained by the States in their state and local air monitoring station (SLAMS) networks as required under 40 CFR Part 58. Further, Appendix C of Part 58 requires that the ambient air monitoring methods used in these EPA-required SLAMS networks must be methods that have been designated by the EPA as either reference or equivalent methods.

Monitoring methods for particulate matter (i.e.,  $PM_{10}$ ) are designated by the EPA as reference or equivalent methods under the provisions of 40 CFR Part 53, which was amended in 1987 to add specific requirements for  $PM_{10}$  methods. Part 53 sets forth functional specifications and other requirements that reference and equivalent methods for each criteria pollutant must meet, along with explicit test procedures by which candidate methods or samplers are to be tested against those specifications. General requirements and provisions for reference and equivalent methods are also given in Part 53, as are the requirements for submitting an application to the EPA for a reference or equivalent method determination. The distinction between reference and equivalent methods is a technical one. On one hand, it provides for detailed, explicit specification of a selected measurement technology for reference methods. On the other hand, it allows alternative (including innovative and potentially improved) methodologies for equivalent methods, based only on meeting specified requirements for functional performance and for comparability to the reference method. For purposes of determining attainment or non-attainment with the NAAQS, however, the distinction between reference and equivalent methods is largely, if not entirely, immaterial.

Under the Part 53 requirements, *reference methods* for  $PM_{10}$  must be shown to use the measurement principle and meet the other specifications set forth in 40 CFR 50, Appendix J (Code of Federal Regulations, 1991). They must also include a  $PM_{10}$  sampler that meets the requirements specified in Subpart D of 40 CFR 53. Appendix J specifies a measurement principle based on extracting an air sample from the atmosphere with a powered sampler that incorporates inertial separation of the  $PM_{10}$  size range particles followed by collection of the  $PM_{10}$  particles on a filter over a 24-h period. The average  $PM_{10}$  concentration for the sample period is determined by dividing the net weight gain of the filter over the sample period by the

total volume of air sampled. Other specifications are prescribed in Appendix J for flow rate control and measurement, flow rate measurement device calibration, filter media characteristics and performance, filter conditioning before and after sampling, filter weighing, sampler operation, and correction of sample volume to EPA reference temperature and pressure. Also, sampler performance requirements in Subpart D of Part 53 include wind tunnel tests for "sampling effectiveness" (the efficacy of the PM<sub>10</sub> particle size separation capability) at each of three wind speeds and "50 percent cutpoint" (the accuracy of the primary 10-micron particle size separation). Field tests for sampling precision and flow rate stability are also specified. In spite of the instrumental nature of the sampler, this method is basically a manual procedure, and all designated reference methods for PM<sub>10</sub> are therefore defined as manual methods.

*Equivalent methods* for PM<sub>10</sub>, alternatively, need not be based on the measurement principle specified in Appendix J nor meet the other Appendix J requirements. Instead, equivalent methods must meet the "sampler" performance specifications set forth in Subpart D of Part 53 and demonstrate *comparability* to a reference method as required by Subpart C of Part 53. The provisions of Subpart C specify that a candidate equivalent method must produce PM<sub>10</sub> measurements that agree with measurements produced by collocated reference method samplers at each of two field test sites. For this purpose, agreement means a regression slope of  $1 \pm 0.1$ , a regression intercept of  $0 \pm 5 \mu\text{g}/\text{m}^3$ , and a correlation  $>0.97$ . These requirements allow virtually any type of PM<sub>10</sub> measurement technique, and therefore an equivalent method for PM<sub>10</sub> may be either a manual method or a fully automated instrumental method (i. e., analyzer).

As of this writing, the EPA has designated seven reference methods and three equivalent methods for PM<sub>10</sub>, as listed in Table 4-1. The reference methods include four methods featuring high-volume samplers from two manufacturers, with one using a cyclone-type size separator and the others using an impaction-type separator. The other reference methods include a low-volume sampler (from a third manufacturer), a low-volume sampler featuring a secondary size separation at 2.5 microns (dichotomous sampler), and a medium-volume, non-commercial sampler. The three designated equivalent methods are all automated PM<sub>10</sub> analyzers and include two operating on the beta-attenuation principle and one based on a tapered element oscillating microbalance (TEOM™). It should be noted that although these latter three automated PM<sub>10</sub> analyzers may be capable of providing continuous or semi-continuous PM<sub>10</sub> concentration

measurements, only 24-h average  $PM_{10}$  measurements are recognized as approved under their equivalent method designations.

#### **4.2.7 Determination of Size Distribution**

The determination of aerosol size distributions can be a powerful research tool when studying source contributions and transformation processes. A number of techniques are available as described by texts such as Willeke and Baron (1993) to make near real-time, single particle aerosol measurement in addition to cascade impactors.

##### **4.2.7.1 Cascade Impactors**

In cascade applications, the aerosol is impacted and trapped onto a series of removable, coated substrates (e.g., greased foils), including a final total stage collection on a filter for gravimetric analysis. Marple et al. (1993) list over 30 single stage and cascade impactors that are either commercially available or still commonly used. The design and calibration of a miniature eight-stage cascade impactor for personal air sampling in occupational settings is described by Rubow et al. (1987), operating at 2.0 lpm. Evaluations of the most commonly used cascade impactor systems have been reported by Vaughan (1989) for the Andersen MK1 and MK2 7-stage cascade impactors, Marple et al. (1991) for the 10-stage Micro-Orifice Uniform Deposit Impactor (MOUDI), and Wang and John (1988) and Hillamo and

**TABLE 4-1. U.S. ENVIRONMENTAL PROTECTION AGENCY-DESIGNATED REFERENCE  
AND EQUIVALENT METHODS FOR PM<sub>10</sub>**

Method No.	Identification	Description	Type	Date
RFPS-1087-062	Wedding & Associates PM Critical Flow High-Volume Sampler.	High-volume (1.13 m <sup>3</sup> /min) sampler with cyclone-type PM <sub>10</sub> inlet; 203 x 254 cm (8 x 10 in) filter.	Manual reference method	10/06/87
RFPS-1287-063	Sierra-Andersen or General Metal Works Model 1200 PM <sub>10</sub> High-Volume Air Sampler System	High-volume (1.13 m <sup>3</sup> /min) sampler with impaction-type PM <sub>10</sub> inlet; 203 x 254 cm (8 x 10 in) filter.	Manual reference method	12/01/87
RFPS-1287-064	Sierra-Andersen or General Metal Works Model 321-B PM <sub>10</sub> High-Volume Air Sampler System	High-volume (1.13 m <sup>3</sup> /min) sampler with impaction-type PM <sub>10</sub> inlet; 203 x 254 cm (8 x 10 in) filter. (No longer available.)	Manual reference method	12/01/87
RFPS-1287-065	Sierra-Andersen or General Metal Works Model 321-C PM <sub>10</sub> High-Volume Air Sampler System	High-volume (1.13 m <sup>3</sup> /min) sampler with impaction-type PM <sub>10</sub> inlet; 203 x 254 cm (8 x 10 in) filter. (No longer available.)	Manual reference method	12/01/87
RFPS-0389-071	Oregon DEQ Medium Volume PM Sampler	Non-commercial medium-volume (110 L/min) sampler with impaction-type inlet and automatic filter change; two 47-mm diameter filters.	Manual reference method	3/24/89
RFPS-0789-073	Sierra-Andersen Models SA241 or SA241M or General Metal Works Models G241 and G241M PM <sub>10</sub> Dichotomous Samplers	Low-volume (16.7 L/min) sampler with impaction-type PM <sub>10</sub> inlet; additional particle size separation at 2.5 micron, collected on two 37-mm diameter filters.	Manual reference method	7/27/89
EQPM-0990-076	Andersen Instruments Model FH62I-N PM <sub>10</sub> Beta Attenuation Monitor	Low-volume (16.7 L/min) PM <sub>10</sub> analyzers using impaction-type PM <sub>10</sub> inlet, 40 mm filter tape, and beta attenuation analysis.	Automated equivalent method	9/18/90

**TABLE 4-1 (cont'd). U.S. ENVIRONMENTAL PROTECTION AGENCY-DESIGNATED REFERENCE  
AND EQUIVALENT METHODS FOR PM<sub>10</sub>**

Method No.	Identification	Description	Type	Date
EQPM-1090-079	Rupprecht & Patashnick TEOM Series 1400 and Series 1400a PM <sub>10</sub> Monitors	Low-volume (16.7 L/min) PM <sub>10</sub> analyzers using impaction-type PM <sub>10</sub> inlet, 12.7 mm diameter filter, and tapered element oscillating microbalance analysis.	Automated equivalent method	10/29/90
EQPM-0391-081	Wedding & Associates PM Beta Gauge Automated Particle Sampler	Low-volume (16.7 L/min) PM <sub>10</sub> analyzer using cyclone-type PM <sub>10</sub> inlet, 32 mm filter tape, and beta attenuation analysis.	Automated equivalent method	3/5/91
RFPS-0694-098	Rupprecht & Patashnick Partisol Model 2000 Air Sampler	Low-volume (16.7 L/min) PM <sub>10</sub> sampler with impaction-type inlet and 47 mm diameter filter.	Manual reference method	7/11/94

Kauppinen (1991) for the 6-stage Berner, low pressure cascade impactor. The smallest particle stages of these impactors can have very small diameter jets and/or very low total pressures to achieve the sub-micron separations. The MOUDI impactor has 2000 holes on the lowest cutpoint stage. Raabe et al. (1988) describe an 8 stage cascade slit impactor with slowly rotating impactor drums instead of flat plates. This arrangement, in combination with a PIXIE analyzer, permitted aerodynamic sizing of elemental components, with temporal resolution. The skill and care required in the operation of cascade impactors suggests that they are research rather than routine samplers.

The importance of the aerosol calibration of a cascade impactor is illustrated by Vaughan (1989) in Figure 4-13, which compares the experimental data with the manufacturer's calibrations and indicates biases as large as  $1.0\ \mu\text{m}$ . Marple et al. (1991) provided a similar type of stage calibration for the MOUDI impactor and included data on the internal particle losses (see Figure 4-14). These loss data showed that an improperly designed inlet to the impactor, combined with the inertial and interception losses of the larger particle sizes, can substantially bias the first stage collections. This was also demonstrated for the inlet to the Andersen impactor by McFarland et al. (1977). Cascade impactors that cover wide particle size ranges inherently require design compromises among competing factors, including cutpoint sharpness, internal stage losses and the physical size of the device.

Cascade impactors can be used to construct distributions of mass and speciated constituents as a function of aerodynamic diameter. These distributions can be constructed graphically or using matrix inversion techniques. Marple et al. (1993) notes that impactor stage calibrations which do not demonstrate sharp cutoffs can cause significant between-stage sizing errors if not accommodated. John et al. (1990) measured distributions over the  $0.08$  to  $16\ \mu\text{m}$  range for mass and inorganic ions for several sites in Southern California. They identified the standard coarse mode and two separate, previously unreported modes in the  $0.1$  to  $1.0\ \mu\text{m}$  range. This latter range was referred to by Whitby (1978) as a single "accumulation" mode. John et al. (1990) described a "condensation" mode at  $0.2 \pm 0.1\ \mu\text{m}$  containing gas phase reaction products, and a "droplet" mode at  $0.7 \pm 0.2\ \mu\text{m}$  which grows from the "condensation" mode by the addition of water and sulfates. Fang et al. (1991) described the effects of flow-induced relative humidity changes on the sizing of acid aerosols in the MOUDI impactor. They noted that it may not be possible to measure size

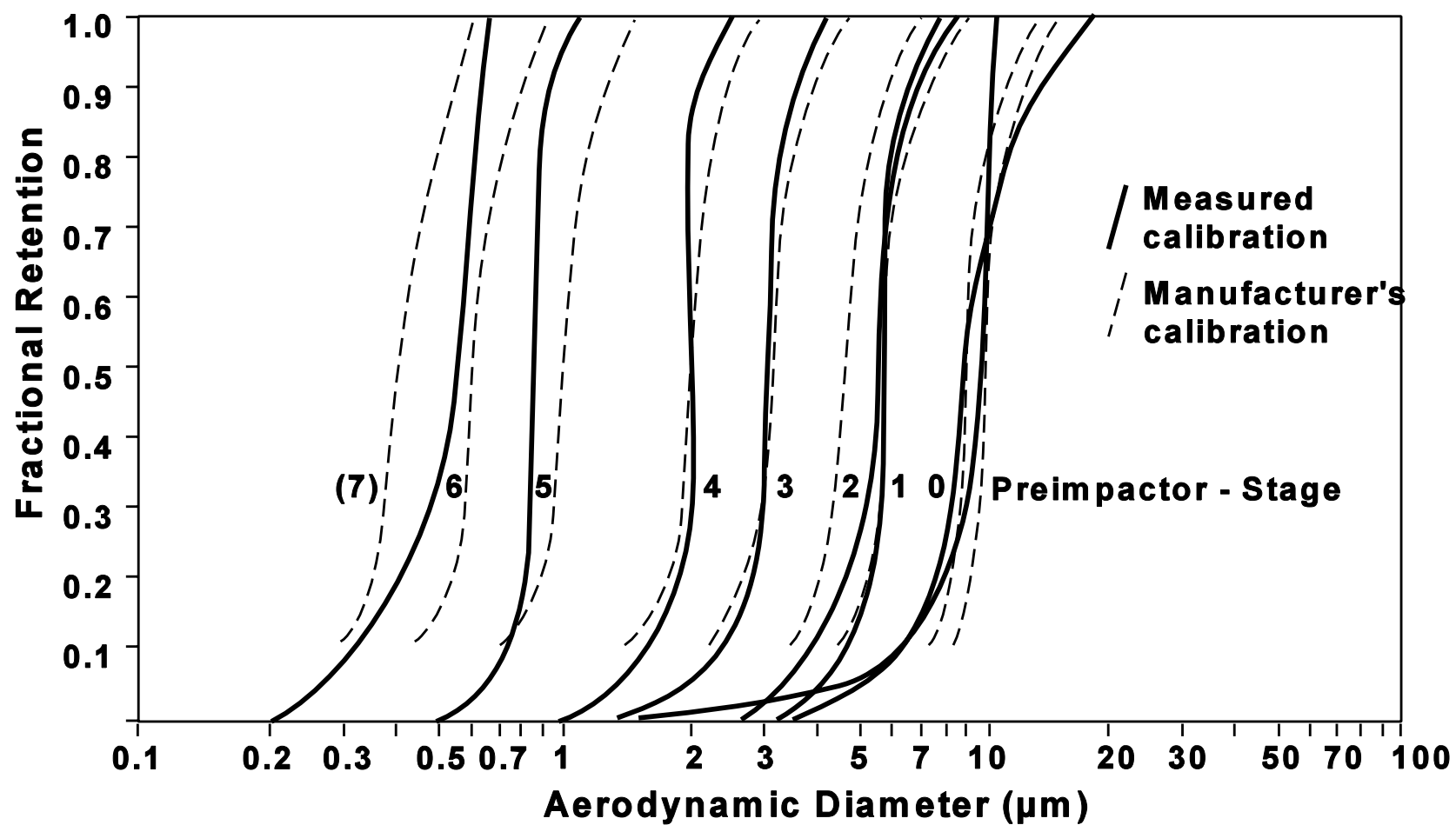


Figure 4-13. Measured calibration of the Andersen Cascade Dupactor as compared to that supplied by the manufacturer.

Source: Vaughan (1989).

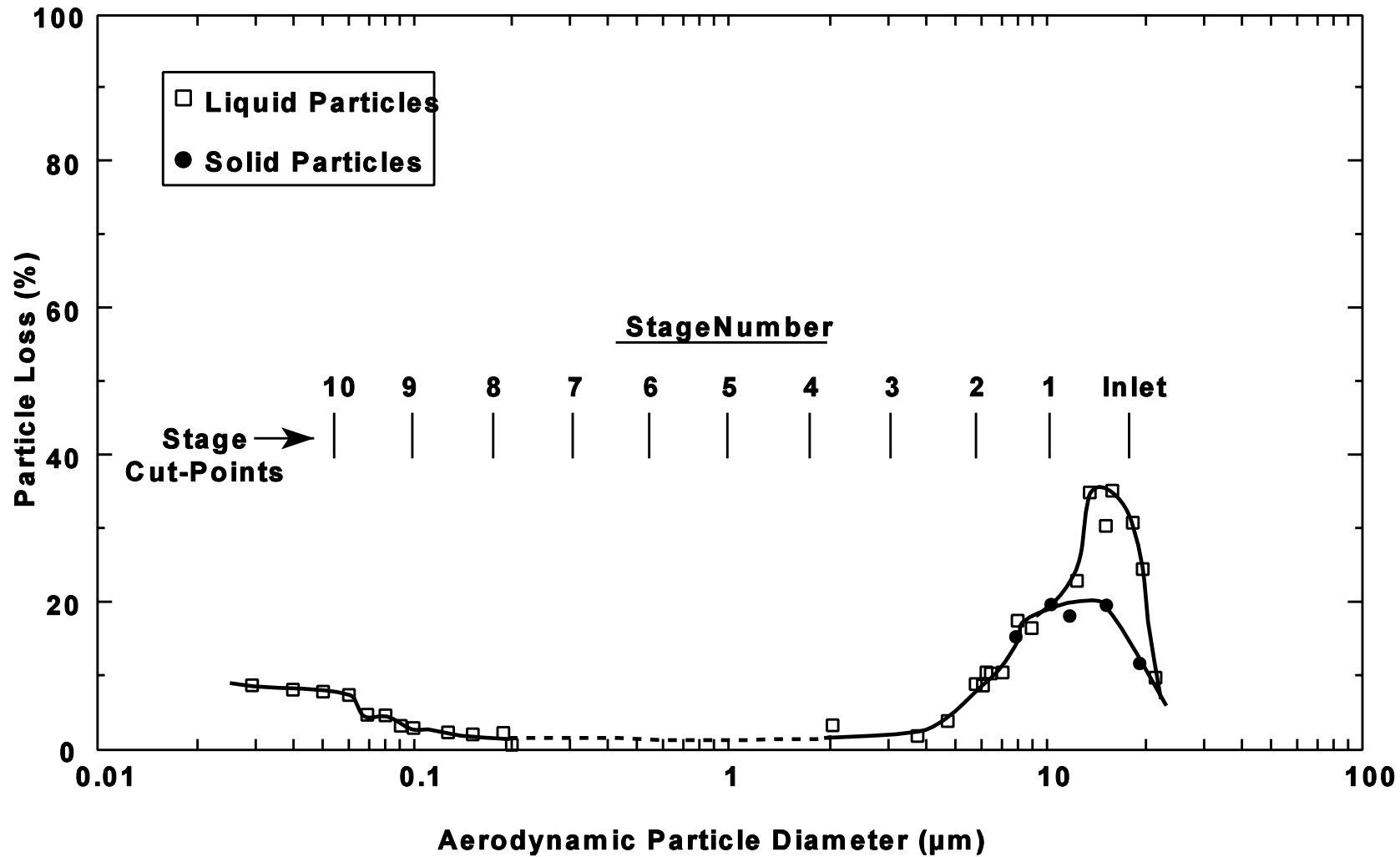


Figure 4-14. Internal losses for the MOUDI impactor.

Source: Marple et al. (1991).



distributions of small (less than about 0.2 to 0.5  $\mu\text{m}$ ) particles with impactors at relative humidities exceeding 80%.

#### **4.2.7.2 Single Particle Samplers**

Aerosol size distribution data are useful for studies of particle transport and transformation processes, source characterization, and particle sizing and collection device performance. In addition to cascade impactors, a number of real time or near real time sizing instruments are available and described in texts such as Willeke and Baron (1993). While cascade impactors provide distributions in terms of aerodynamically sized mass, single particle sampling devices can produce optically sized distributions as a function of particle number (count), with surface area and volume distributions computed during the data reduction, assuming spherical particles. Particle density and shape information as a function of size are required to convert from volume distributions to an estimated mass basis. Individual particle sizing and counting instruments are generally limited to a particle detection range of a decade or so, but several devices can overlap to cover the range of approximately 0.001 to 10  $\mu\text{m}$ . The principle of detection of an instrument restricts the particle sizes which can be detected. For example, instruments using electrical mobility analysis are limited to particle sizes less than about 1  $\mu\text{m}$ . Optical methods are typically used to measure particles larger than about 0.1 to 0.3  $\mu\text{m}$ . Inlet and transport system losses of coarse particles above about 2  $\mu\text{m}$ , prior to the sensing volume, must be factored into reported size distributions.

The three most commonly used single particle sampler types are aerodynamic particle sizers, electrical mobility analyzers and optical particle counters (OPC's). Aerodynamic particle sizers use laser doppler anemometry to measure the velocity of particles in a jet. The acceleration of the particle is related to the aerodynamic particle diameter. This technique is typically applied to particles larger than about 0.5  $\mu\text{m}$ . In electrical mobility analysis, aerosol with a known charge distribution flows through an electric field. The particles migrate according to their mobility which can be related to size. The original TSI electrical aerosol analyzer (EAA) performed this separation in an integrated manner over the total size distribution and detected the particles by unipolar diffusion charging. A more versatile approach, the differential mobility analyzer or DMA (Liu et al., 1978), is able to examine a narrow slice of the size distribution in an equilibrium charge state, detected by a condensation

nucleus counter (CNC). Differential mobility analyzers have been employed in pairs (Tandem Differential Mobility Analyzer, or TDMA) to examine both (a) particle characteristics such as  $\text{NH}_3$  and  $\text{H}_2\text{SO}_4$  reaction rates (McMurry et al., 1983) and (b) the sensitivity of the size distributions of Los Angeles aerosol to relative humidity (McMurry and Stolzenburg, 1989). The latter research used the first DMA to select particles of known mobility from the input aerosol, a humidification system to condition the selected particles, and the second DMA to determine mobility changes. Optical particle counters pass a jet of aerosol through an optical system. Light scattered from individual particles is detected and the signal is processed in a multi-channel analyzer. Discrete signals are counted and sorted by intensity and by optical size. One example of a forward-scattering counter with an open sensing volume (for use on aircraft) is the Particle Measuring Systems, Inc., FSSP-300, which can provide high resolution (31 channel) count distributions over the size range of 0.3 to 20  $\mu\text{m}$  (Rader and O'Hern, 1993). Gebhart (1993) described currently available OPC's and their counting efficiencies over a range of diameters.

Single particle samplers have common considerations, as discussed below.

Calibration: They are calibrated with reference aerosol either by the manufacturer or by the user. If the properties of the aerosol measured are quite different than the calibration, the indicated size distribution may be quite different than actual distribution. Brockman et al. (1988) demonstrated that the APS calibration can vary significantly with the type of test aerosol and showed substantial response biases between oleic acid and polystyrene latex spheres above 10  $\mu\text{m}$ . Wang and John (1989) described a procedure to correct the APS response for aerosol particle density. Particle shape can also provide serious sizing errors, and specific calibrations are needed for particles with shape factors significantly different from unity (spherical). Yeh (1993) commented that the calculated geometric standard deviations ( $\sigma_g$ ) determined by the EAA and DMA are generally larger than 1.3, even if the correct value is significantly closer to unity. Woskie et al. (1993) observed, as did Willeke and Degarmo (1988), that optical particle counting devices must be appropriately calibrated using realistic aerosols, especially for low concentration applications. Harrison and Harrison (1982) suggested that the ratio of fine particle mass concentration to optical scattering extinction will be more variable when a significant contribution is made by irregular (shaped) particles - an event likely to occur when the mean mass diameter exceeds 1  $\mu\text{m}$ .

Particle Concentration Effects: Gebhart (1993) noted that the response of single particle counters may be influenced by extremely high particle concentrations. Wake (1989) and Heitbrink et al. (1991) described the coincidence problems of the APS when sampling high total particle concentrations, especially for sizes greater than 1  $\mu\text{m}$ . Baron et al. (1993) reported that the concentration levels giving 1% coincidence in an aerodynamic particle sizer for 0.8, 3 and 10  $\mu\text{m}$  particles, respectively, are the relatively low values of 558, 387 and 234 particles/ $\text{cm}^3$ . Optical particle counters can experience coincidence errors (two particles are detected as a single particle) and counter saturation at high particle concentrations. Hinds and Kraske (1986) described the performance of the PMS, Inc. LAS-X and noted a sizing accuracy of  $\pm 2$  channel widths, with coincidence errors of less than 10% for concentrations below 10,000 particles/ $\text{cm}^3$ . Clearly, typical particle concentrations found in the atmosphere may produce significant errors if sample dilution is not utilized.

#### **4.2.8 Automated Sampling**

Automated methods to provide measures of aerosol concentrations in the air have existed for decades in an attempt to provide temporal definition of suspended particles and enhance every-sixth-day sampling schedules with a minimum labor expense. Arnold et al. (1992) collected daily 24-h  $\text{PM}_{10}$  samples with an automated monitor and noted that 80% of the highest 10 daily concentrations between 1989 and 1990 were not encountered by the every-sixth-day sampling schedule. Some of the automated samplers (e.g., British Smoke Shade and AISI tape samplers) described in the 1982 Criteria Document were indicator measures of aerosol concentration, using calibrations relating aerosol concentrations to reflected or absorbed light. Tape samplers were used in the U. S. primarily as exceedance (index) monitors.

The beta attenuation and integrating nephelometer techniques described in the 1982 Criteria Document primarily were research methods. Since that time, the beta gauge sampling approach has been refined and a new approach, based on the Tapered Element Oscillating Microbalance (TEOM) principle, has been developed. Samplers based on these techniques have been designated as equivalent methods for  $\text{PM}_{10}$ .

Although one could be readily constructed, there are presently no commercially available, automated high volume ( $> 1 \text{ m}^3/\text{min}$  flowrate) aerosol samplers, excluding the possibility of the timed operation of an array of manual samplers. The physical size of such a sampling system

using 8 x 10 inch filters is impractical. The dichotomous sampler is currently the only low volume, gravimetrically-based sampler commercially available in an automated version.

#### **4.2.8.1 Smoke Shade (British Smoke, Black Smoke)**

Historically, the British smoke shade sampler was one of the earliest ambient PM sampling devices to be developed and to gain widespread use as an automated optical PM monitoring method. Key features and limitations of the British or black smoke (BS) method were discussed in EPA's 1982 Criteria Document. As indicated in Chapters 3 and 14 of that Criteria Document, the BS method typically involves use of a sampler that draws ambient air through an inverted funnel and approximately 3m of plastic tubing to deposit collected particles on white filter paper. The amount of PM deposited during a given time period (e.g., 1-h during severe episodes, or more typically, 24-h) is determined by measuring the blackness of the stain on the filter paper. An automated version of the sampler can collect daily samples sequentially for up to eight days.

It is important to note, as described in the 1982 Criteria Document, that the BS method and its variations (e.g., the OECD version) in routine use typically employ standard monitoring equipment with a  $D_{50}$  cutpoint=4.5  $\mu\text{m}$ , which mainly allows fine-mode particles and small coarse mode particles (some ranging up to ~8 to 10  $\mu\text{m}$ ) to be collected. Thus, regardless of whether larger particles are present in the atmosphere, the BS method collects predominately small particles. Also, the BS method neither directly measures mass nor determines chemical composition of the collected PM. Rather, it measures light absorption of particles as indicated by reflectance from the stain formed by the particles collected on the filter paper, which depends both on the density of the stain, or amount of PM collected, and the optical properties of the collected PM. Smoke particles composed of elemental carbon, found in incomplete fossil-fuel combustion products, typically make the greatest contribution to the darkness of the stain, especially in urban areas. Thus, the amount of elemental carbon, but not organic carbon, present in the stain tends to be most highly correlated with BS reflectance readings. Other nonblack, noncarbon particles also have optical properties such that they can affect the reflectance readings, although their contribution to optical absorption is usually negligible.

Since the relative proportions of atmospheric carbon and noncarbon PM can vary greatly from site to site or from one time to another at the same site, the same absolute BS reflectance reading can be associated with markedly different amounts (or mass) of collected particles or, in

unusual circumstances, even with markedly different amounts of carbon. Site-specific calibrations of reflectance readings against actual mass measurements obtained by collocated gravimetric monitoring devices are therefore necessary to obtain estimates of atmospheric concentrations of particulate matter based on the BS method. A single calibration curve relating mass or atmospheric concentration (in  $\mu\text{g}/\text{m}^3$ ) of particulate matter to BS reflectance readings obtained at a given site may serve as a basis for crude estimates of the levels of PM (mainly small particles) at that site over time, so long as the chemical composition and relative proportions of elemental carbon and noncarbon PM do not change substantially. However, the actual mass or smoke concentrations present at a particular site may differ markedly (by factors of two or more) from the values calculated from a given reflectance reading on either of the two most widely used standard curves (the British and OECD standard smoke curves)<sup>9</sup>. Thus, great care must be taken in interpreting the meaning of any BS value reported in terms of  $\mu\text{g}/\text{m}^3$ , especially as employed in the British and other European epidemiological studies discussed in Chapter 12 of this document.

There has existed long standing interest with regard to relationships between ambient PM concentrations indexed by BS readings (based on conversion of reflectance values to estimated  $\mu\text{g}/\text{m}^3$  concentrations by means of standard calibration curves) and those obtained by gravimetric methods. The 1982 Criteria Document noted that Ball and Hume (1977) and Waller (1963) found that such relationships are site, season, and particle-source dependent. Also, Lee et al. (1972) noted, from collocated TSP hi-vol and smoke shade sampler comparisons made at various sites in England, that the overall correlation coefficients between these measurements for all sites was 0.618. However, the individual coefficients ranged from 0.936 (good correlation) to 0.072 (no correlation). Bailey and Clayton (1980) showed that smoke shade measurements correlated more closely with soot (elemental carbon) content than with gravimetric mass. Other work by Paschel and Egner (1981) and Clayton and Wallin (1982) showed consistently higher TSP values than BS readings (converted to  $\mu\text{g}/\text{m}^3$ ) from collocated samplers in various U.S. and

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<sup>9</sup>For this reason, smoke data reported in  $\mu\text{g}/\text{m}^3$  based on either the British or OECD Standard curve are appropriately interpreted in terms of "nominal"  $\mu\text{g}/\text{m}^3$  smoke units and cannot be accepted as accurate estimates of airborne PM mass unless corroborated by local site-specific gravimetric calibrations. In other words, unless based on local site-specific calibrations, smoke readings in  $\mu\text{g}/\text{m}^3$  cannot yield quantitative estimates of atmospheric PM concentrations. In the absence of such calibrations, smoke readings only allow for rough qualitative (i.e., < ; = ; or >) comparisons of amounts of PM present at a given time versus another time at the same site and do not permit meaningful comparisons between PM levels at different geographic areas having airborne PM of different chemical composition (especially in terms of relative proportions of elemental carbon).

U.K. cities, respectively (as would be expected given that the BS measurements of fine and small coarse mode particles typically represent only some fraction of the wider range of particles sampled by TSP measurements). Clayton and Wallin (1982), not surprisingly, also found widely variable ratios of TSP to BS readings from different U.K. cities reflecting the varying proportions of small particles present in the total ambient mix of particles at different sites. Likewise, varying (site- and season-dependent) relationships between BS measurements and ambient PM measurements made by various gravimetric methods have been reported in the Federal Republic of Germany (Laskus, 1983) and in the semi-arid climate of Baghdad, Iraq (Kanbour et al., 1990). Lastly, Muir and Laxton (1995) reported that, for Bristol (a moderate size U.K. city), daily average BS (averaged over six urban background sites) appears to be a reasonable predictor of daily average  $PM_{10}$  and daily 1-h peak  $PM_{10}$  values; but different relationships apply for winter versus summer, indicating that BS and  $PM_{10}$  measure different components of airborne PM (i.e., BS may be a better index of fine-mode particles than  $PM_{10}$ , which has a  $D_{50}$  cutpoint of  $\approx 10 \mu m$ ).

Only limited examples exist of derivation of models of interrelationships between BS readings and gravimetric measurements for particular time periods in a given location. For example, see Mage (1995) for discussion of an empirical model relating BS to TSP values during London winters of the 1950s and 1960s.

#### **4.2.8.2 Coefficient of Haze (AISI/ASTM Tape Sampler)**

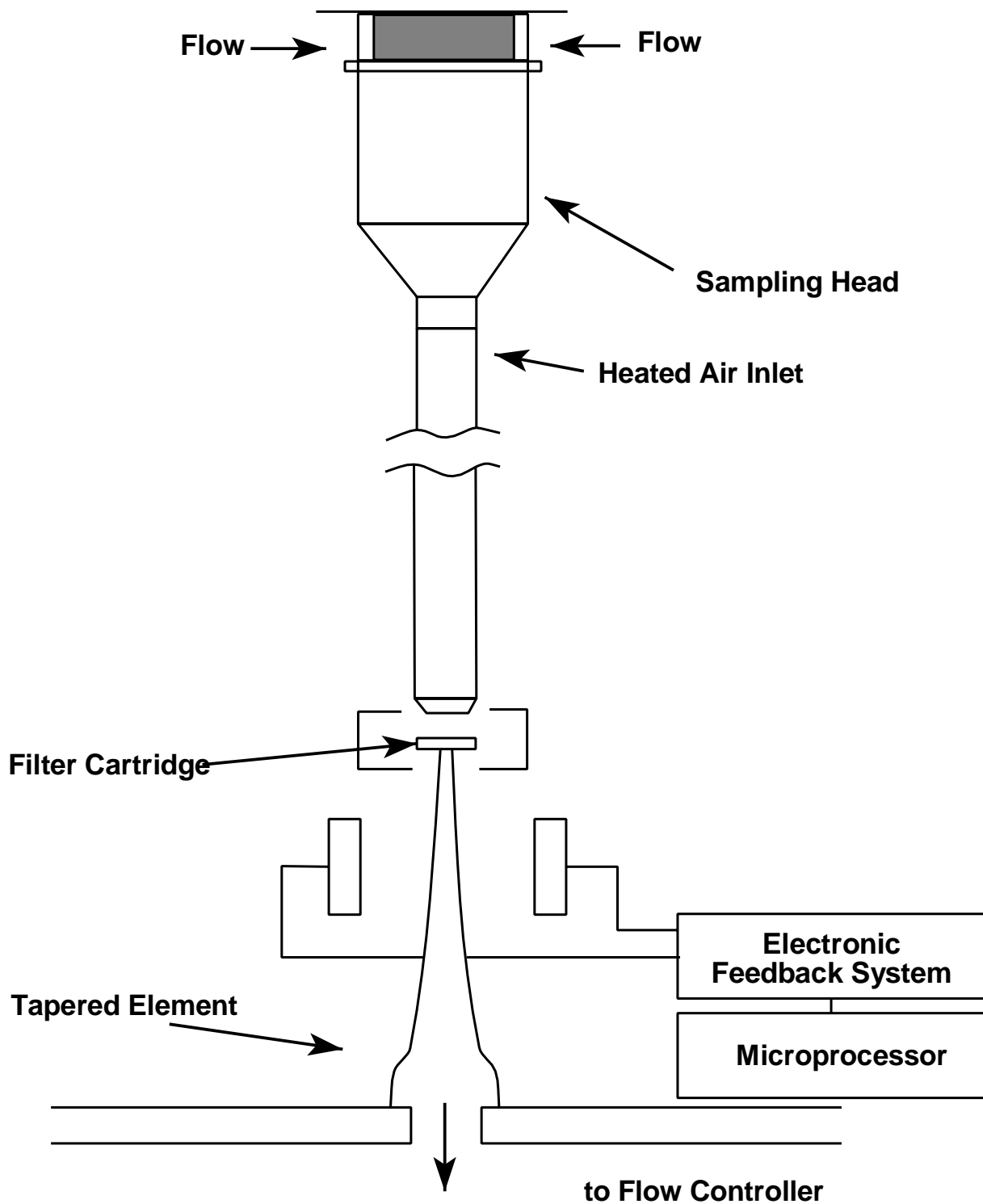
The 1982 Criteria Document also described a second type of automated optical PM measurement methods. Developed before 1940, the American Iron and Steel Institute (AISI) light transmittance method is similar in approach to the BS technique and has been employed for routine monitoring in some American cities. The instrument collects particles with a  $D_{50}$  cutpoint of  $\approx 5.0 \mu m$  aerodynamic diameter and uses an air intake similar to that of the BS method. Ambient PM is collected on a filter-paper tape that is periodically advanced to allow accumulation of another stain. Opacity of the stain is determined by transmittance of light through the deposited material and the tape. The results are expressed in terms of optical density or coefficient of haze (CoH) units per 1,000 linear feet of air sampled (rather than in mass units). Readings in CoH units are somewhat more responsive to noncarbon particles than are BS measurements; but, again, the AISI method neither directly measures mass nor determines

chemical composition of the PM collected. Any attempt to relate CoHs to  $\mu\text{g}/\text{m}^3$  requires site-specific calibration of CoH readings against mass measurements determined by a collocated gravimetric device, but the accuracy of such mass estimates are still subject to question.

Few attempts have been reported on calibration of COH measurements versus results from collocated gravimetric devices. One notable attempt (Ingram, 1969; Ingram and Golden, 1973) was reported for New York City, but the results are of very limited applicability to New York City aerometric data of the 1960's. Also, Regan et al. (1979) showed that CoH readings correlate favorably with gravimetric measurements limited to smaller particle sizes. Edwards (1980) and Edwards et al. (1983) have also shown that BS reflectance measurements can be related to the absorption coefficient of the atmosphere and that BS measurements can be converted to approximate CoH measurements made by AISI tape sampler using the absorption coefficient relationships. As several investigators noted, (e.g., Lodge, et al., 1981), if a relationship could be developed between optical and gravimetric measurements, it would be site specific, but still variable because of seasonal and long-term differences in the sources of collected particle size fractions and their carbon content.

#### **4.2.8.3 TEOM® Sampler**

The Tapered Element Oscillating Microbalance (R & P, Inc.) sensor, as described by Patashnick and Rupprecht (1991), consists of an oscillating tapered tube with a filter on its free end (see the diagram in Figure 4-15). The change in mass of the filter and collected aerosol produces a shift in the oscillation frequency of the tapered tube that is directly related to mass. Rupprecht et al. (1992) suggested that the filter can be archived after sampling for



**Figure 4-15. Rupperecht and Patashnick TEOM® sampler.**  
Source: Patashnick and Rupperecht (1991).



subsequent analysis. The sampler inlet has a PM<sub>10</sub> cutpoint and operates at 16.67 lpm. A flow splitter samples a 3 lpm portion of this flow to be filtered. Since the fraction of volatile species (e.g., water, nitrates, organics) in the aerosol is a function of ambient temperature, the TEOM® sampler heats the inlet air stream to a constant 30 or 50 °C to keep moisture in the vapor phase. The mass transducer is also heated to 50 °C to stabilize the measurement process. Operation with the flow stream heated to a lower temperature (e.g., 30 °C) is possible, but care must be taken to avoid moisture condensation that will confound the measurement. The transducer is also heated to 50 °C to stabilize the mass measurement. A factory calibration regression is used to electronically correct the computed mass from the TEOM® sampler to that measured by a reference PM<sub>10</sub> sampler.

Although several studies (e.g. Patashnick and Rupprecht, 1991; Kalhoff and Crumpler, 1990) have shown consistent and linear relationships between the TEOM® sampler and gravimetric PM<sub>10</sub> samplers, a number of studies have shown biases under certain conditions. Several researchers, including Cahill et al. (1994), Hering (1994) and Meyer et al. (1992) have reported that the modification of the aerosol by the elevated operating temperature appears to have a significant effect (loss) on mass concentration. Meyer et al. (1992) collocated a TEOM® sampler with an PM<sub>10</sub> SA1200 gravimetric sampler in Mammoth Lakes, CA during a winter heating season (heavy wood stove usage). The regressions between the TEOM® sampler and PM<sub>10</sub> sampler gave strong correlations ( $r^2 > 0.98$ ), with slopes of 0.55 for operation at 50 °C, and 0.66 for operation at 30 °C. The negative bias of the TEOM was attributed primarily to losses of semi-volatile organics from the filter. Cahill et al. (1994) reported that the TEOM® sampler showed biases on the order of 30% low and poor correlations with PM<sub>10</sub> samplers in dry, dusty conditions. The reasons for this discrepancy were unknown. The field comparison data of Patashnick and Rupprecht (1990) showed near unity ( $1 \pm 0.06$ ) regression slopes for the TEOM with the Wedding IP<sub>10</sub> and Sierra-Andersen dichotomous samplers in El Paso, TX and Birmingham, AL. Since aerosol composition is highly dependent on local sources and meteorology, volatilization losses could be expected to be site- and season-dependent. This could significantly affect the rigor of collocated field sampling. A WESTAR (1995) council report summarizes the relationships between TEOM® monitors and other direct gravimetric samplers in at least 10 states in the western U.S. This report concluded that on average the TEOM® sampler concentrations were 21.8% lower than other collocated PM<sub>10</sub> samplers for

concentrations  $> 50 \mu\text{g}/\text{m}^3$ . This would significantly affect the TEOM® sampler's ability to be used as a "trigger" monitor for control strategy plans. More data are needed to determine the implications of these problems on the ability of the TEOM® sampler to be used in a regulatory setting. Although it is clear that the TEOM® sampler can provide  $\text{PM}_{10}$  data comparable to the existing reference method samplers, the specific field sampling conditions where excessive bias might be expected to occur have not been completely defined. A portion of the bias is undoubtedly due to concomitant variabilities in the associated gravimetric measurements.

#### **4.2.8.4 Beta Gauge**

The Andersen FH 62I-N beta attenuation sampler was described by Merrifield (1989) and uses a 30 mCi Krypton-85 source and detector to determine the attenuation caused by deposited aerosols on a filter (see diagram in Figure 4-16). To improve the stability over time, a reference reading is periodically made of a foil with an attenuation similar to that of the filter and collected aerosol. The Wedding beta attenuation sampler was described by Wedding and Weigand (1993) and uses a 100 mCi  $^{14}\text{C}$  source. Both samplers have inlets with a  $\text{PM}_{10}$  cutpoint, with the Andersen sampler operating at 16.67 lpm and the Wedding at 18.9 lpm. The filter material is contained on a roll and advances automatically on a time sequence, or when a preset aerosol loading is reached. An automatic beta gauge sampler was also described by Spagnolo (1989), using a  $15 \mu\text{m}$  inlet and a  $^{14}\text{C}$  source. The calibration of a beta gauge is site specific, and a calibration regression must be processed electronically to provide accurate mass readings. Rupprecht et al. (1992) suggested that the closer link between deposited mass and frequency shift for the TEOM principle should provide less site-specific response, compared to the aerosol compositional sensitivity of the beta gauge technique.

Arnold et al. (1992) provided data over a 2 year period in Denver, CO for the mass concentration regression data from a Wedding beta gauge, showing a range of correlations ( $r^2$  from 0.72 to 0.86), varying by sampler and season. The authors suggested that installation of a newer technology beta gauge accounted for the higher correlations, but noted that unexplained outliers resulted in poorer than expected results. The regression slopes between the two sampler types showed that the beta gauge averaged 19% lower than a

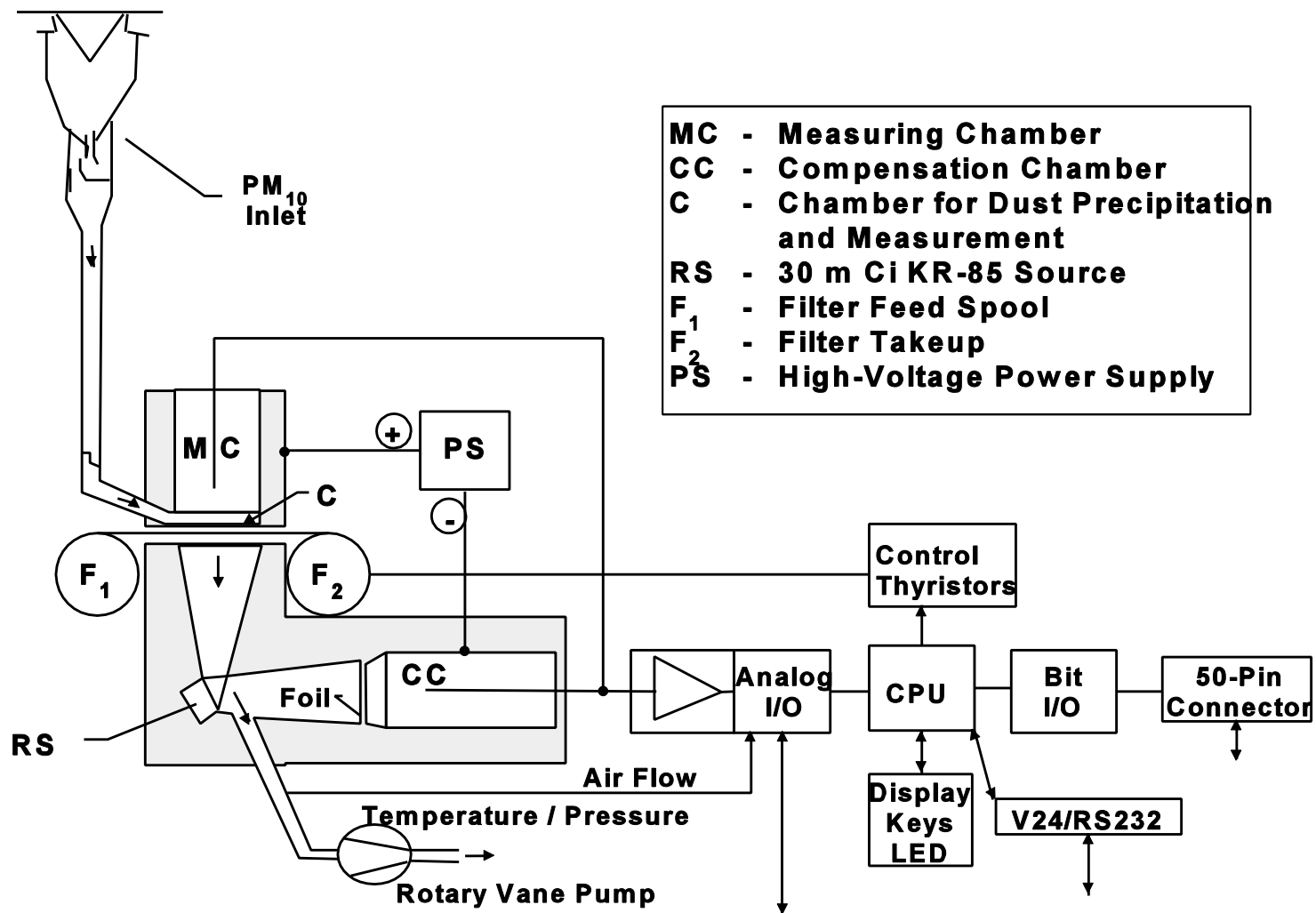


Figure 4-16. Andersen beta gauge sampler.

collocated Wedding PM<sub>10</sub> gravimetric sampler. It should be noted that the Wedding PM<sub>10</sub> inlet has typically been reported (see Section 4.2.2.4) to be 10 to 15% lower in collocated field tests with Sierra-Andersen PM<sub>10</sub> inlets. A WESTAR (1995) council report summarizes the relationships between beta gauge monitors and other direct gravimetric samplers in at least five states in the western U.S. This report concluded that on average beta gauge concentrations were 8.6% lower than other collocated PM<sub>10</sub> samplers for concentrations > 20  $\mu\text{g}/\text{m}^3$ . Field data from Wedding and Weigand (1993) at two sites (Fort Collins, CO and Cleveland, OH) using the same samplers produced regressions exhibiting strong correlations ( $r^2 = 0.99$ ) with no apparent outliers and a composite slope of 1.00. Arnold et al. (1992) operated the PM<sub>10</sub> high volume samplers on the required every-6th-day schedule and the beta attenuation monitors continuously, and noted that only 22.5% of the exceedance days, as measured by the beta monitor, were operational days for the high volume samplers.

#### **4.2.8.5 Nephelometer**

The integrating nephelometer is commonly used as a visibility monitor; it measures the light scattered by aerosols, integrated over as wide a range of angles as possible. A schematic diagram of the integrating nephelometer is shown in Figure 4-17 (from Hinds, 1982). The measured scattering coefficient of particles,  $b_{sp}$ , can be summed with the absorption coefficient,  $b_{ap}$ , and the comparable coefficients for the gas phase to compute the overall atmospheric extinction coefficient,  $b_{ext}$ . Methods for estimating absorption and extinction for atmospheric particles are discussed in 8.2.2. The atmospheric extinction has been related to visibility as visual range. The particle scattering coefficient is dependent upon particle size, index of refraction and illumination wavelength, as shown by Charlson et al. (1968) in Figure 4-18, while the absorption coefficient is relatively independent of size. The field calibration of nephelometers has historically been based on the refractive index of Freon-12 (and occasionally carbon dioxide), but newer calibration procedures using atomized sugar aerosols have been proposed (Horvath and Kaller, 1994) as more environmentally conscious. Nephelometry over a narrow wavelength band or at a selected wavelength can be applied to measure the laser light scattered from a volume of aerosol containing a number of

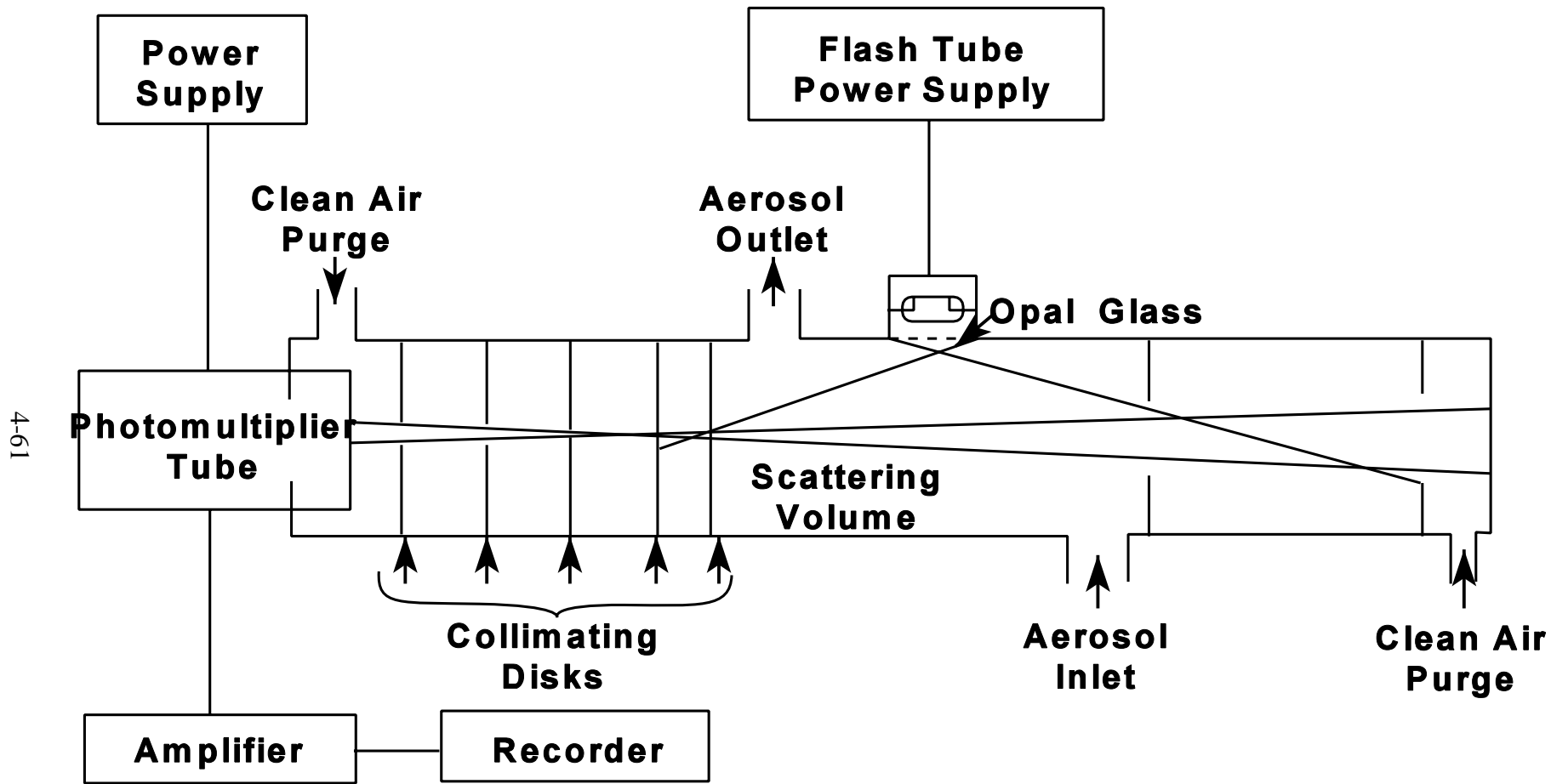
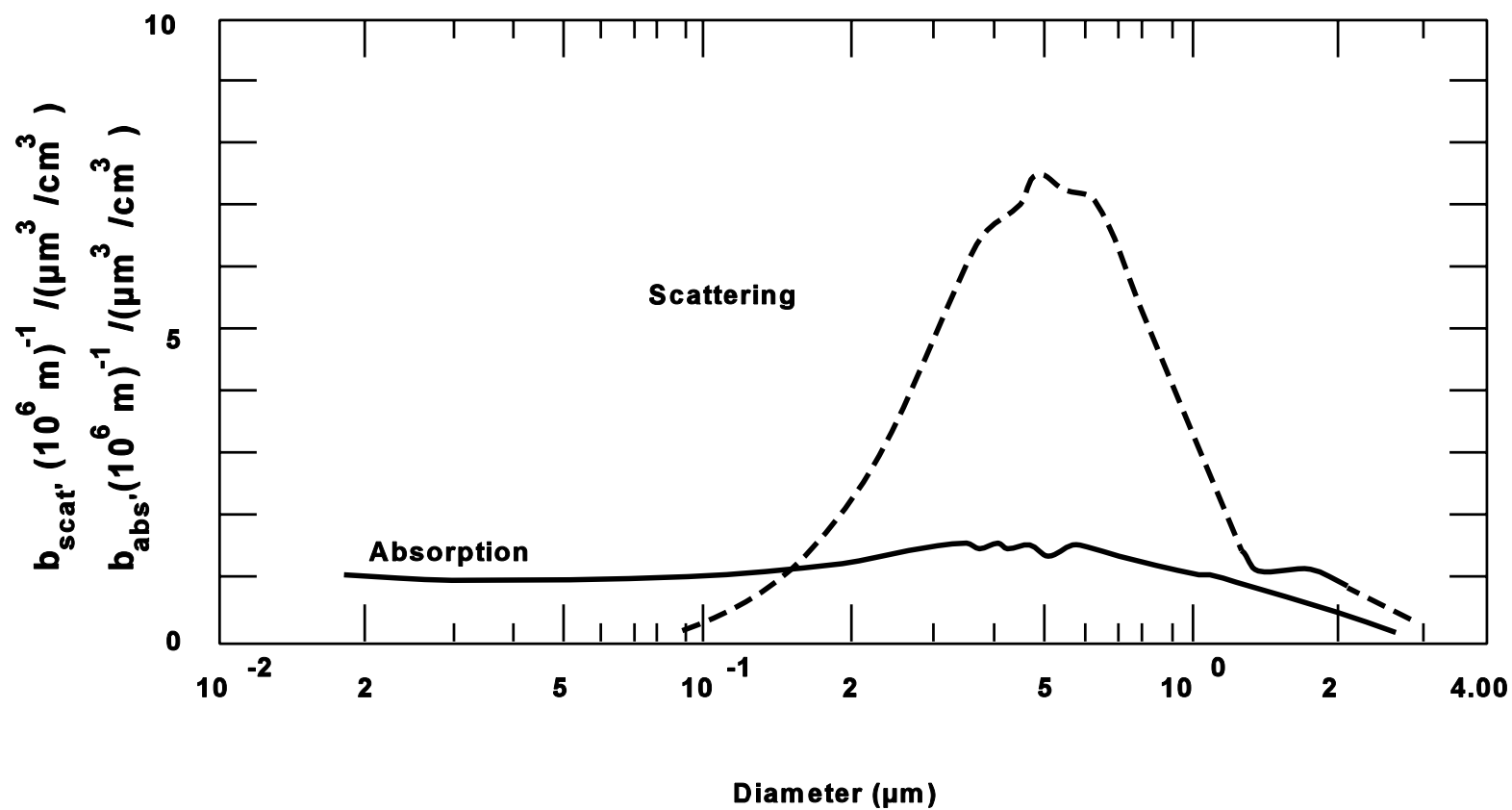


Figure 4-17. Integrating nephelometer.



**Figure 4-18.** Particle-scattering coefficient per volume concentration as a function of particle size for spherical particles of refractive index 1.5 illuminated by 550 nm light.

Source: Charlson et al. (1968).

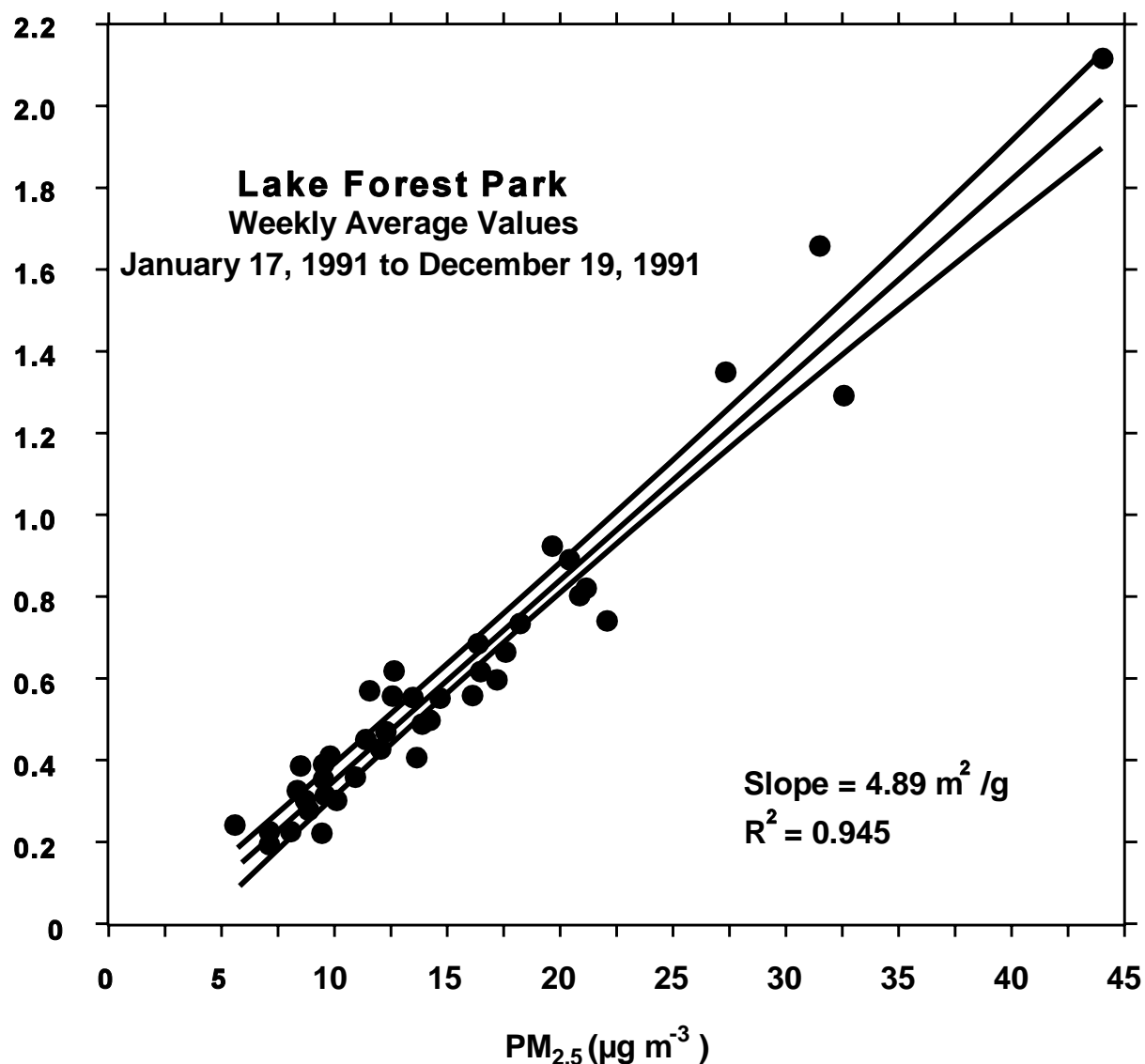
particles. Gebhart (1993) described devices such as the MIE, Inc.<sup>10</sup>. MINIRAM, often used in portable applications to estimate real-time aerosol concentrations. Cantrell et. al. (1993) showed that MINIRAM calibration was significantly different for diesel and mine aerosols. Woskie et al. (1993) described the performance of a MINIRAM (using the manufacturer's calibration) against gravimetric borate concentrations for particles as large as 30  $\mu\text{m}$ , and found significant biases (a regression slope = 4.48). This bias was expected, since the large mass median particle diameters were substantially outside the respirable particle range recommended by the manufacturer.

The relative insensitivity of the nephelometer to particles above  $\sim 2 \mu\text{m}$  results in poor correlations with  $\text{PM}_{10}$  mass. Larson et al. (1992) showed strong correlations ( $r^2 = 0.945$ ) between  $b_{\text{sp}}$  and fine fraction mass (see Figure 4-19) for a woodsmoke impacted neighborhood near Seattle, WA, with a slope of  $4.89 \text{ m}^2/\text{g}$ . They noted that this slope fell within the range of values reported by others and was predicted by Mie scattering theory. The slope of the Larson et al. (1992) data could be compared with other site-specific calibrations, such as the data of Waggoner and Weiss (1980), which gave a composite slope of  $3.13 \text{ m}^2/\text{g}$ , characterized by the authors as representative of a "wide range" of sites. Lewis (1981) provided an analysis of the relationships of the features of the ambient size distribution to  $b_{\text{sp}}$ . The inlet air stream to the nephelometers for the latter data was heated from 5 to 15  $^{\circ}\text{C}$  above background. Rood et al. (1987) conducted a controlled comparison of the influence of aerosol properties on  $b_{\text{sp}}$  in Riverside, CA and reported a regression slope against fine mass (defined as less than  $2.0 \mu\text{m}$ ) of  $2.1 \text{ m}^2/\text{g}$  with an  $r^2$  value of 0.92. In this experiment, the relative humidity for  $b_{\text{sp}}$  determinations was controlled to less than 35% and the gravimetric filter substrate was nylon. The authors attributed the smaller than normal slope reading to possible nitrate evaporation from the filtered aerosol and artifact reactions with the nylon substrate material. Thomas et al. (1993) demonstrated that the influence of relative humidity on the relationship between photometer response and collocated gravimetric particle concentrations can be predicted.

The data scatter in Figure 4-19 (if assumed to be typical of such comparisons) would suggest that fine particle mass concentration estimates from  $b_{\text{sp}}$  values were typically within 5 to 7  $\mu\text{g}/\text{m}^3$  of the gravimetrically determined values. To be useful as a surrogate measure

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<sup>10</sup>Bedford, MA.



**Figure 4-19. Correlation of  $b_{sp}$  and fine fraction mass.**

Source: Larson et al. (1992).

for mass concentration, the site-specific nephelometer calibration should be valid for a wide range of situations, especially during episodes where the concentration levels approach or exceed an action limit. The scattergram of  $b_{sp}$  versus fine particle mass provided by Rood et al. (1987) showed much greater variability, with a given  $b_{sp}$  value providing an estimated 20 to 25  $\mu\text{g}/\text{m}^3$  concentration range. They noted that metastable  $\text{H}_2\text{O}$  contributed 5 to 20% of the total particle light scattering coefficient, especially during the late afternoon and early evening. The



precisions and biases of the dependent and independent variables between  $b_{sp}$  and fine mass concentration are not constants, since at least one factor - moisture content of the aerosol - affects both measures. The gravimetric sample filters are typically equilibrated to a specific relative humidity range (e.g., 40 to 60%) to normalize the tare weighings.

Sloane (1986) and others have noted that light scattering from particles is not solely a function of mass but are also very dependent on a summation of the scattering coefficients of each species. The scattering cross section of a particle is dependent on the water content, and, hence, the relative humidity in situ. Pre-heating of the inlet air of the nephelometer normalizes the response to water content, but biases the reading relative to the in situ case. Sloane (1986) also gave the computed and measured scattering coefficients for ammonium sulfate and noted that chemical interactions can cause a two-fold variation in scattering response to a change in the mass of hygroscopic constituents. It was also observed that the light scattering efficiency of an aerosol such as ammonium acid sulfate is not a constant, but varies with the overall aerosol composition. Eldering et al. (1994) developed and validated a predictive model for  $b_{sp}$  in Southern California. This model used composite size distributions constructed from a TSI, Inc.<sup>11</sup> EAA, a PMS, Inc.<sup>12</sup> LAS-X and a Clime, Inc.<sup>13</sup> multi-channel OPC, and filter-based estimates of refractive indices for ammonium sulfate, ammonium nitrate, organic carbon, elemental carbon and residual aerosol mass concentrations as independent variables. The quality of their comparisons with nephelometer data suggested that this approach could be used to test models that predict visual range from source emissions. Further research is needed to determine the effectiveness of the integrating nephelometer as a predictor of fine particle mass concentrations.

## **4.2.9 Specialized Sampling**

### **4.2.9.1 Personal Exposure Sampling**

The application of aerosol measurement technologies to smaller and less obtrusive samplers have resulted in devices used as fixed-location indoor aerosol samplers and personal exposure monitors (PEMs) worn on the body to estimate exposure. The reduction in physical size of personal aerosol sampling systems to reduce participant burden sometimes results in

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<sup>11</sup>Minneapolis, MN.

<sup>12</sup>Boulder, CO.

<sup>13</sup>Redlands, CA.

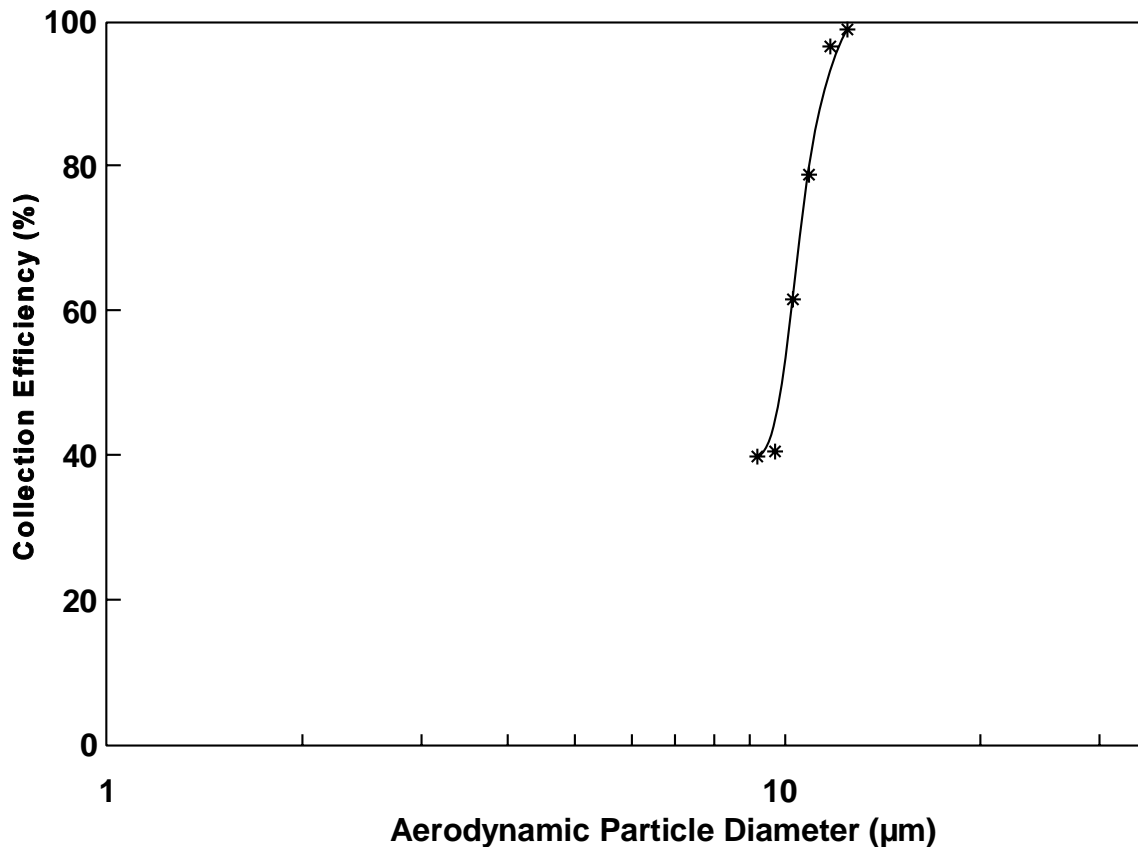
poorer aerosol collection performance as compared to the outdoor counterparts. Wiener and Rodes (1993) noted that personal sampling systems generally have poorer precisions than outdoor aerosol samplers, due to the smaller sampler collections (from lower flowrates) and poorer flow controllers. Özkaynak et al. (1993) reported that the precisions of collocated PEMs in the PTEAM study operating at 4.01 pm for a 12-h period were 3 to 4% (RSD). Wallace et al. (1994) reported biases for the Particle Total Exposure Assessment Methodology study averaging a factor of two between personal exposure measurements and fixed location PM<sub>10</sub> concentrations. He was unable to completely account for the biases, but attributed portions to proximity to indoor sources, a difference in inlet cutpoints (11.7  $\mu\text{m}$  versus 10.0  $\mu\text{m}$ ) and the collection of aerosols from the "personal cloud" caused by body dander. Rodes et al. (1991) showed that the ratio of personal to indoor aerosol measurements for the EPA PTEAM study appeared to be log-normally distributed with a median value of 1.98 and an unexpectedly high value of 3.7 at the 90th ("most exposed") percentile. Ingham and Yan (1994) suggested that the performance of a personal aerosol sampling inlet in an isolated mode (without mounting on a representative humanoid bluff body) can result in substantial under-sampling for larger particles. The relationship between measured aerosol exposure at some external location on the body and actual uptake through oral and nasal entry is very complex.

Buckley et al. (1991) described the collection efficiency of an MSP, Inc.<sup>14</sup> personal aerosol sampler at 4.0 lpm as shown in Figure 4-20. They evaluated this sampler in a field comparison study with collocated PM<sub>10</sub> high volume and dichotomous samplers. The precision for the personal sampler was found to be very good ( $\text{CV} = \pm 3.2\%$ ) with strong correlations ( $r^2 = 0.970$ ) with the dichotomous samplers. Liroy et al. (1988) described a similar comparison for a 10 lpm Air Diagnostics and Engineering, Inc.<sup>15</sup> indoor air sampler, with a PM10 inlet characterized by Marple et al. (1987). Correlations against the PM10 dichotomous sampler were also described as very strong ( $r^2 > 0.970$ ), but noted a substantial bias caused by the loss of fragments from indoor air sampler's glass fiber filters. They recommended that exposure studies using samplers that collect small total volumes should utilize filters with greater integrity, such as Teflon. Colome et al. (1992) describe an

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<sup>14</sup>Minneapolis, MN.

<sup>15</sup>Naples, ME.



**Figure 4-20. Collection efficiency of the MSP personal aerosol sampler inlet.**

Source: Buckley et al. (1991).

indoor/outdoor sampling study using an impactor characterized by Marple et al. (1987) with a  $PM_{10}$  cutpoint that had duplicate impactors with the same cutpoint in series. This sequential arrangement, in combination with a coating of 100  $\mu$ l of light oil, was used to minimize particle bounce at 4.0 lpm for 24 h period.

Personal aerosol sampler systems have typically been characterized as burdensome (excessive weight, size, noise). The success of passive detector badges for gaseous pollutants has recently prompted research into passive aerosol samplers. Brown et al. (1994) described a prototype aerosol sampler utilizing electrostatic charge to move the particles to a collection substrate. They noted that preliminary results are encouraging, but the effective sampling rate and size-selectivity of the sampler was dependent on the electrical mobility of the aerosol. This posed calibration problems for real aerosols with a distribution of electrical mobility's.

Holländer (1992) described a passive pulsed-corona sampler that has similar collection characteristics as a  $PM_{10}$  inlet, with only modest wind speed dependence.

The performance characterization of PEMs has been considered for occupational settings by Kenny and Lidén (1989), who reviewed the ACGIH, National Institute for Occupational Safety and Health (NIOSH), and EPA  $PM_{10}$  aerosol sampler performance programs. They proposed that an international consensus be reached on the basic principles underlying the experimental protocols for testing personal samplers, as an essential prerequisite to the setting of standards. An ISO working group has made progress in developing such a consensus (Kenny, 1992). As EPA becomes more focused on exposure assessment and personal exposure sampling, it will become even more important for the agency to consider establishing performance specifications for personal aerosol samplers.

Models have become powerful tools in understanding aerosol behavior in the vicinity of personal exposure samplers. This is demonstrated by particle trajectory models that can predict the influences of the geometries and flow field on aerosol capture and losses (e.g., Okazaki and Willeke, 1987, Ingham and Yan, 1994, and Tsai and Vincent, 1993). These models have not only permitted more rapid design changes to accommodate new cutpoints and flowrates, but have added insights as to the influence of air flow obstructions on sampling efficiencies. Vincent and Mark (1982) suggested that there is a critical particle trajectory that determines whether a particle is sampled or rejected by an inlet worn on the body. An extension of this model applicable to personal exposure sampling by Ingham and Yan (1994) suggested that testing the performance of a personal aerosol sampling inlet in an isolated mode (without mounting the inlet on a representative bluff body) can result in under-sampling for larger particles by a factor of two. Validation of this model may explain a portion of the bias reported by Wallace et al. (1994) between personal and indoor sampler measurements.

#### **4.2.9.2 Receptor Model Sampling**

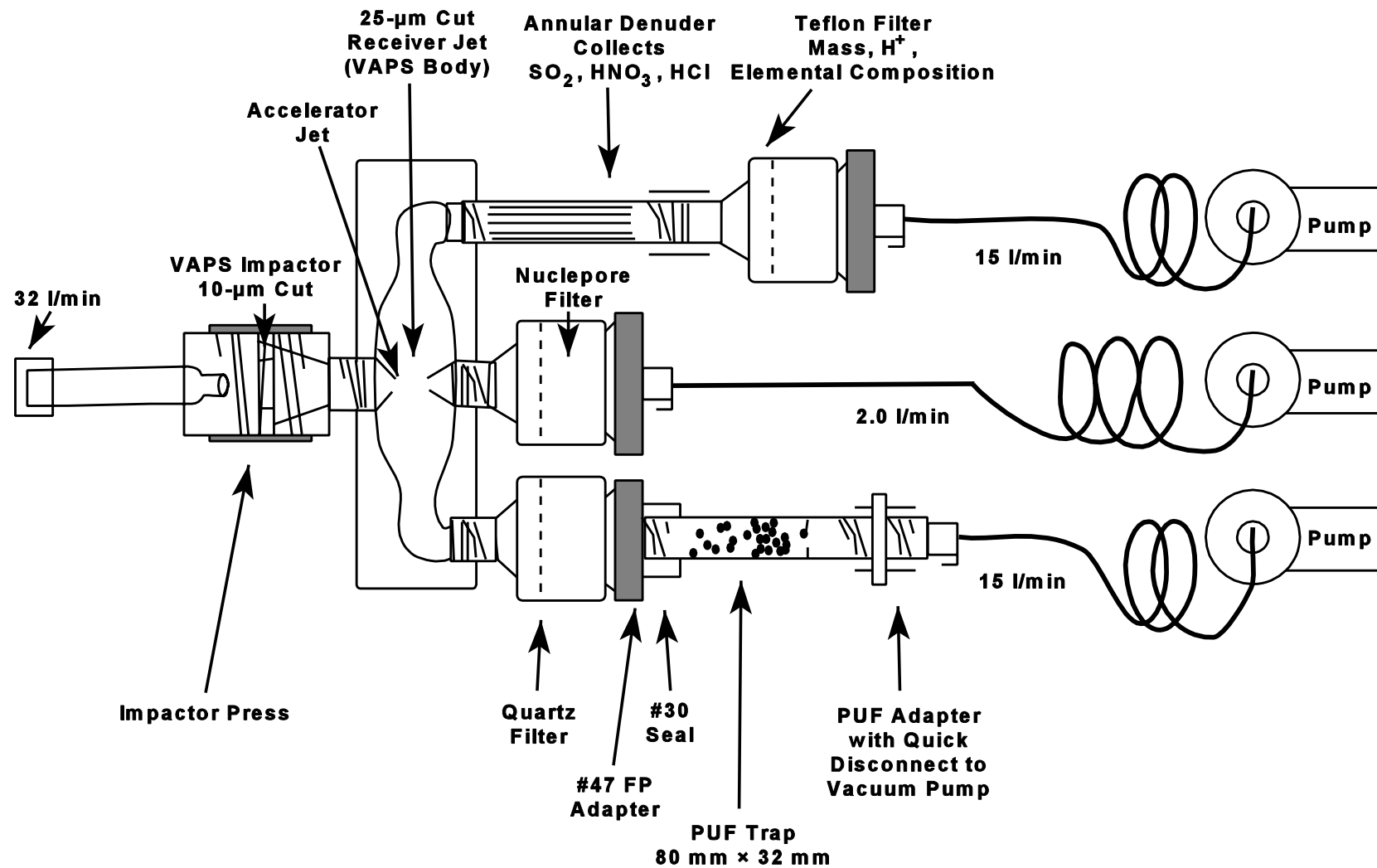
Receptor modeling has become an established tool to relate ambient concentrations of pollutants to major source categories, by apportioning the components in collected ambient aerosol samples using complimentary source "signatures". Various approaches developed for constructing source/receptor relationships were described by Henry et al. (1984), who also provided a review of modeling fundamentals. They listed the advantages and disadvantages of

multivariate models and discussed multi-collinearity problems associated with the presence of two or more sources with nearly identical signatures. Javitz et al. (1988) described the basic Chemical Mass Balance (CMB) approach and showed the influence of the variance in identifying a component in the source signature sample on the projected apportionment. Dzuby et al. (1984) described aerosol source and receptor collection schemes that permitted the separation of ambient samples into fine and coarse fractions for mass, elemental and volatile carbon, and metals analyses. Stevens and Pace (1984) suggested the addition of Scanning Electron Microscopy to permit additional categorization using x-ray diffraction analysis. The most widely used aerosol receptor model is the EPA CMB 7.0 model described by Watson et al. (1990). This paper describes the structure of the model and computer code and the data requirements to evaluate the validity of the estimates. Numerous papers have been published describing the applications of receptor models to the apportionment of the sources of aerosols, with the receptor modeling conference summary by Watson et al. (1989b) descriptive of the state-of-the-art.

Stevens et al. (1993) described (see Figure 4-21) a modified dichotomous sampler with a  $PM_{10}$  inlet, two Fine channels operating at 15 lpm and one coarse channel operating at 2.0 lpm, designated as the Versatile Air Pollution Sampler (VAPS). The additional fine fraction channel permitted sampling on a 47 mm Teflon filter for elemental analysis and a 47-mm quartz filter for carbon speciation (elemental and volatile). A Nuclepore filter was used on the Coarse channel for Scanning Electron Microscopy (SEM) evaluation and energy dispersive x-ray diffraction analysis for selected particles.

#### **4.2.9.3 Particle Acidity**

An emphasis was placed on sampling sulfuric acidic aerosols in the 1982 Criteria Document. This was followed by a number of research efforts (e.g., Ferm, 1986; Koutrakis et al., 1988; Pierson et. al., 1989) to identify and study the in situ rate reactions, develop sampling strategies to representatively remove the acid particle from the air, identify the co-existing reactive species (e.g., ammonia, nitric acid, aerosol sulfates and nitrates), and protect the collected aerosol prior to analysis. A "Standard" and an "Enhanced" method were subsequently described (U.S. Environmental Protection Agency, 1992) for the



**Figure 4-21. Modified dichotomous sampler (VAPS).**

Source: Stevens et al. (1993).

determination of aerosol acidity (titratable H<sup>+</sup>) using annular denuder technology. The "Standard" method did not account for potential interferences from nitric acid, ammonium nitrate aerosol, or other ammonium salts. The "Enhanced" method added an additional denuder prior to filtration, with nylon and treated glass fiber backup filters to account for these species. These sampling technologies utilized either an inlet impactor or a cyclone with 2.5  $\mu\text{m}$  cutpoints to sample the fine fraction. This technology has recently been extended to other reactive aerosol systems, including semi-volatile organics (e.g., Vossler et al., 1988). Bennett et al. (1994) describe a PM<sub>2.5</sub> cyclone-based, filter pack sampling system designed for fine particle network sampling and acidity measurements, as part of the Acid MODES program. The sampler operated at 8.8 lpm, and was designed to selectively remove ammonia, speciate gas and particle phase sulfur compounds, as well as collect gas phase nitric acid. An intercomparison of 18 nitric acid measurement methods was reported by Hering et al. (1988), who noted that measurements differed by as much as a factor of four and biases increased as nitric acid loadings increased. In general the filter pack systems reported the highest acidity measurements, while the denuder-difference techniques reported significantly lower measurements. Benner et al. (1991) in a comparison of the SCENES filter pack sampler with a denuder-based sampler found excellent agreement between sampler types for both nitric acid and total nitrates. They attributed the close agreement to limited positive artifact formation, since the test field site had high nitric acid gas to particulate nitrate ratios. John et al. (1988) noted that internal aluminum sampler surfaces denude nitric acid, and describe the design of an aluminum denuder for the inlet of a commercially available dichotomous sampler to quantitatively remove nitric acid for extended periods.

Brauer et al. (1989) describe the design of a miniature personal sampler to collect acid aerosols and gases. A significant finding was the lower than expected personal acidity levels, attributed to the "personal cloud" production of ammonia by the body. Personal exposure levels of acid aerosols were reported to be lower than indoor measurements.

## **4.2.10 Measurement Method Comparisons**

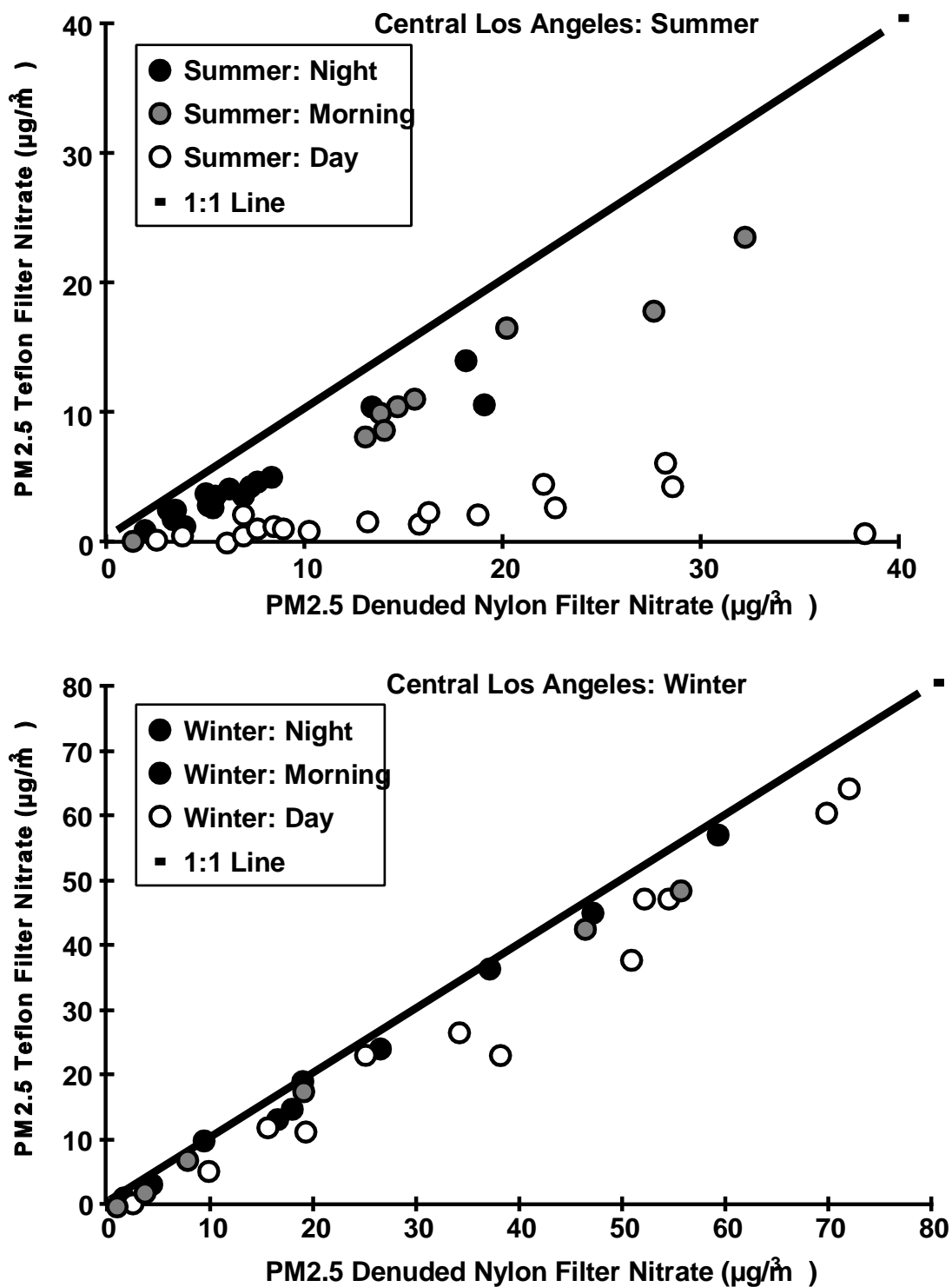
### **4.2.10.1 Nitrate**

Methods for measuring particle nitrate and gaseous nitric acid were compared in the field as part of the 1985 Nitrogen Species Methods Comparison Study conducted over an 8-day

period in the summer of 1985 in Claremont, CA (Hering et al., 1988). Particle nitrate methods included sampling with filter packs (teflon and nylon filters operated in series), sampling with nylon or impregnated filters operated downstream of a denuder to remove vapor nitric acid (Possanzini et al., 1983; Shaw et al., 1982; Appel et al., 1981), and sampling with an impactor (Wall et al., 1988). Results from that study showed that the precision for identical samplers was about 4% (Anlauf et al., 1988; Solomon et al., 1988). Denuded nylon filter methods were used in 6 different samplers operated by 4 different groups (Appel et al., 1988; John et al., 1988; Pierson et al., 1988; Solomon et al., 1988). Data from these 6 methods show no systematic bias among samplers. The average measurement precision (coefficient of variation) was 11%. Impactor results were also in agreement with that from the denuded nylon filters (Wall et al., 1988). In contrast, fine particle nitrate values from teflon filter of the filter packs were 43 to 59% lower than those measured by denuded nylon filters, with higher discrepancies for longer sampling times (Soloman et al., 1988). The lower results on filter pack sampling are due to the volatilization of nitrate particles from the filter. The vaporized nitrate is measured as nitric acid on the backup filter (Hering et al., 1988; Solomon et al., 1988). To summarize, sampling with denuded nylon filters or with impactors gave equivalent values for fine particle nitrate, whereas teflon filter sampling was biased low due to the volatilization losses.

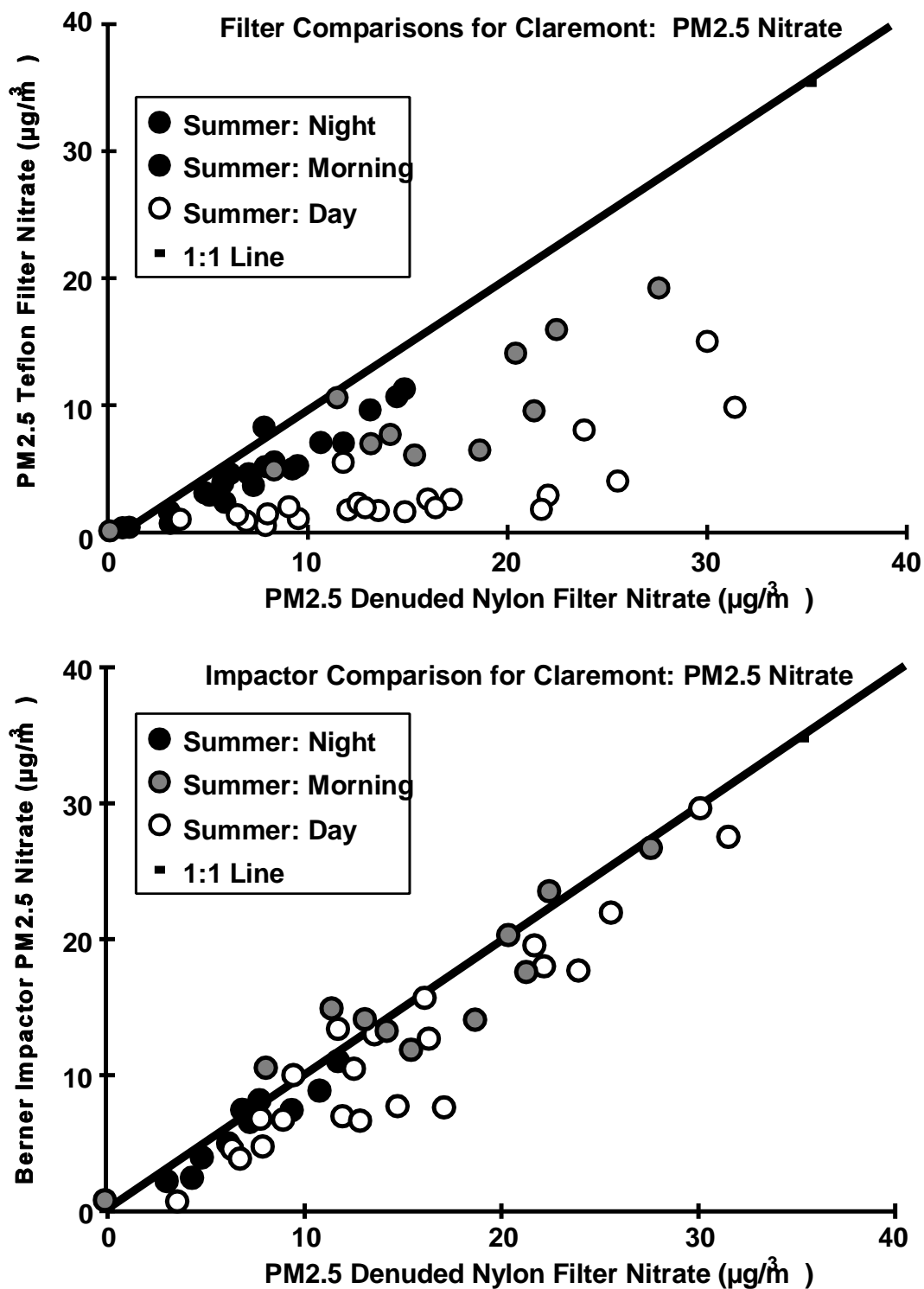
The results of the 1985 Nitrogen Species Methods Comparison Study were confirmed by data collection as part of the 1987 Southern California Air Quality Study (Chow et al., 1994). In this study, sampling times were 4 to 7 h. Samples were retrieved immediately, within 30 minutes of the end of sampling. Fine particle samples were collected by teflon filters, by denuded nylon filters and by impactors. Results, stratified by time of day and season, are illustrated in Figures 4-22 and 4-23 for central Los Angeles, CA and Claremont, CA, respectively. Losses from the teflon filters are greatest in the summer, especially for daytime samples (10 a.m. to 2 p.m., and 2 p.m. to 6 p.m.). Over 11 summer sampling days at 8 basin locations for Claremont, CA, an average of 79% or  $9.9\mu\text{g}/\text{m}^3$  of the fine particle nitrate was volatilized from the teflon filters for summer daytime sampling. For nighttime and morning samples, 40% was lost. The percentage losses are smaller for winter samples, but the absolute magnitude remains high at  $8.9\mu\text{g}/\text{m}^3$  for daytime samples. Impactor data are in much closer agreement with those from the denuded nylon filter than the teflon filter.





**Figure 4-22. Comparison of PM<sub>2.5</sub> nitrate mass measurements from Teflon® filter versus denuded nylon filter sample collection for Los Angeles, CA.**

Source: Chow, et al. (1994).



**Figure 4-23. Comparison of PM<sub>2.5</sub> nitrate mass measurements from Teflon® filter versus denuded nylon filter sample collection for Claremont, CA.**

Source: Chow, et al. (1994).

#### **4.2.10.2 Carbonaceous Particulate Matter**

Methods for measuring carbonaceous aerosol, classified as either "organic" or "black" carbon, were compared in a similar study conducted in the summer of 1986 in Glendora, CA (Hering et al., 1990). In that study, analytical methods were compared, as were differences in simultaneous ambient sampling of PM<sub>2.5</sub> aerosol with quartz filters, adsorption-corrected quartz filters and two types of impactors. The results showed generally good agreement among analytical methods for total carbon, with 5 of the 6 laboratories reporting values within 9% of each other. In contrast, ambient sampling results showed variations among methods. Quartz filter results, whether or not corrected for carbon vapor adsorption were within 40% of each other. Concentrations from impactors, exclusive of after-filter, were lower than the mean from the filter samplers by as much as 50%. Addition of the after-filter carbon brought impactor values to within 10% of the mean, but the lack of "black" carbon on these after-filters leads to the conclusion that vapor adsorption led to a positive bias for quartz filter sampling on these days. Similar results were found for the 1987 Southern California Air Quality Study, for which impactor measurements of carbon were systematically lower than filter measurements (Chow, et al., 1994).

### **4.3 ANALYSIS OF PARTICULATE MATTER**

The interest in the composition of aerosol particles lies in the areas of: (1) explaining and inventorying the observed mass, (2) establishing the effect of aerosols on health and welfare, and (3) attributing ambient aerosols to pollution sources. While any compositional measurement will address one or more of these goals, certain methods excel for specific tasks. In general, no single method can measure all chemical species, and comprehensive aerosol characterization programs use a combination of methods to address complex needs. This allows each method to be optimized for its objective, rather than be compromised to achieve goals unsuitable to the technique. Such programs also greatly aid quality assurance objectives, since confidence may be placed in the accuracy of a result when it is obtained by two or more methods on different substrates and independent samplers.

In the sections that follow, some of the more commonly used methods that address the goals stated above are described. The sections are designed to be illustrative rather than

exhaustive, since new methods are constantly appearing as old methods are being improved. These chemical analysis methods for the following section are divided into four categories: (1) mass, (2) elements, (3) water-soluble ions, and (4) organics. Material balance comparing the sum of the chemical species to the PM mass concentrations show that elements, water soluble ions, and organic and elemental carbon typically explain 65 to 85% of the measured mass and are adequate to characterize the chemical composition of measured mass for filter samples collected in most urban and non-urban areas. Some of these chemical analysis methods are non-destructive, and these are preferred because they preserve the filter for other uses. Methods which require destruction of the filter are best performed on a section of the filter to save a portion of the filter for other analyses or as a quality control check on the same analysis method. Table 4-2 identifies the elements and chemical compounds commonly found in air using these methods with typical detection limits.

Less common analytical methods, which are applied to a small number of specially-taken samples, include isotopic abundances (Jackson, 1981; Currie, 1982; Hirose and Sugimura, 1984); mineral compounds (Davis, 1978, 1980; Schipper et al., 1993); and functional groups (Mylonas et al., 1991; Palen et al., 1992; 1993; Allen et al., 1994). Recent advances in infrared optics and detectors have resulted in the quantitative determination of the major functional groups (e.g., sulfate, nitrate, aliphatic carbons, carbonyl carbons, organonitrates, and alcohols) in the atmospheric aerosol (Allen et al., 1994). The advantages of functional analysis in source apportionment are that the number of functional groups is much less than the number of organic compounds to be classified. The cited references provide information on sampling and analysis methods for these highly-specialized methods.

The following section focuses on:

- Physical analysis of elements and single particle size, shape, and composition,
- Wet chemical analysis of anions and cations, and
- Organic analysis of organic compounds and elemental/organic carbon.

**TABLE 4-2. INSTRUMENTAL DETECTION LIMITS FOR  
PARTICLES ON FILTERS**

Minimum Detection Limit in ng/m <sup>3a</sup>									
	ICP/ AES <sup>b,d</sup>	AA Flame <sup>b,d</sup>	AA Furnace <sup>b</sup>	INAA <sup>b,f</sup>	PIXE <sup>g</sup>	XRF <sup>c</sup>	IC <sup>b</sup>	AC <sup>b</sup>	TOR <sup>b</sup>
Be	0.06	2 <sup>d</sup>	0.05	NA <sup>h</sup>	NA	NA	NA	NA	NA
Na	NA	0.2 <sup>d</sup>	< 0.05	2	60	NA	NA	NA	NA
Mg	0.02	0.3	0.004	300	20	NA	NA	NA	NA
Al	20	30	0.01	24	12	5	NA	NA	NA
Si	3	85	0.1	NA	9	3	NA	NA	NA
P	50	100,000	40	NA	8	3	NA	NA	NA
S	10	NA	NA	6,000	8	2	NA	NA	NA
Cl	NA	NA	NA	5	8	5	NA	NA	NA
K	NA	2 <sup>d</sup>	0.02	24	5	3	NA	NA	NA
Ca	0.04	1 <sup>d</sup>	0.05	94	4	2	NA	NA	NA
Sc	0.06	50	NA	0.001	NA	NA	NA	NA	NA
Ti	0.3	95	NA	65	3	2	NA	NA	NA
V	0.7	52	0.2	0.6	3	1	NA	NA	NA
Cr	2	2	0.01	0.2	2	1	NA	NA	NA
Mn	0.1	1	0.01	0.12	2	0.8	NA	NA	NA
Fe	0.5	4	0.02	4	2	0.7	NA	NA	NA
Co	1	6 <sup>d</sup>	0.02	0.02	NA	0.4	NA	NA	NA
Ni	2	5	0.1	NA	1	0.4	NA	NA	NA
Cu	0.3	4	0.02	30	1	0.5	NA	NA	NA
Zn	1	1	0.001	3	1	0.5	NA	NA	NA
Ga	42	52	NA	0.5	1	0.9	NA	NA	NA
As	50	100	0.2	0.2	1	0.8	NA	NA	NA
Se	25	100	0.5	0.06	1	0.6	NA	NA	NA
Br	NA	NA	NA	0.4	1	0.5	NA	NA	NA
Rb	NA	NA	NA	6	2	0.5	NA	NA	NA
Sr	0.03	4	0.2	18	2	0.5	NA	NA	NA
Y	0.1	300	NA	NA	NA	0.6	NA	NA	NA
Zr	0.6	1000	NA	NA	3	0.8	NA	NA	NA
Mo	5	31	0.02	NA	5	1	NA	NA	NA
Pd	42	10	NA	NA	NA	5	NA	NA	NA
Ag	1	4	0.005	0.12	NA	6	NA	NA	NA
Cd	0.4	1	0.003	4	NA	6	NA	NA	NA
In	63	31	NA	0.006	NA	6	NA	NA	NA
Sn	21	31	0.2	NA	NA	8	NA	NA	NA

**TABLE 4-2 (cont'd). INSTRUMENTAL DETECTION LIMITS FOR**

## PARTICLES ON FILTERS

Minimum Detection Limit in ng/m <sup>3a</sup>									
Species	ICP/ AES <sup>b,d</sup>	AA Flame <sup>b,d</sup>	AA Furnace <sup>b</sup>	INAA <sup>b,f</sup>	PIXE <sup>g</sup>	XRF <sup>c</sup>	IC <sup>b</sup>	AC <sup>b</sup>	TOR <sup>b</sup>
Sb	31	31	0.2	0.06	NA	9	NA	NA	NA
I	NA	NA	NA	1	NA	NA	NA	NA	NA
Cs	NA	NA	NA	0.03	NA	NA	NA	NA	NA
Ba	0.05	8 <sup>d</sup>	0.04	6	NA	25	NA	NA	NA
La	10	2,000	NA	0.05	NA	30	NA	NA	NA
Au	2.1	21	0.1	NA	NA	2	NA	NA	NA
Hg	26	500	21	NA	NA	1	NA	NA	NA
Tl	42	21	0.1	NA	NA	1	NA	NA	NA
Pb	10	10	0.05	NA	3	1	NA	NA	NA
Ce	52	NA	NA	0.06	NA	NA	NA	NA	NA
Sm	52	2,000	NA	0.01	NA	NA	NA	NA	NA
Eu	0.08	21	NA	0.006	NA	NA	NA	NA	NA
Hf	16	2,000	NA	0.01	NA	NA	NA	NA	NA
Ta	26	2,000	NA	0.02	NA	NA	NA	NA	NA
W	31	1,000	NA	0.2	NA	NA	NA	NA	NA
Th	63	NA	NA	0.01	NA	NA	NA	NA	NA
U	21	25,000	NA	NA	NA	1	NA	NA	NA
Cl <sup>-</sup>	NA	NA	NA	NA	NA	NA	50	NA	NA
NO <sub>3</sub> <sup>-</sup>	NA	NA	NA	NA	NA	NA	50	NA	NA
SO <sub>4</sub> <sup>-</sup>	NA	NA	NA	NA	NA	NA	50	NA	NA
NH <sub>4</sub> <sup>+</sup>	NA	NA	NA	NA	NA	NA	NA	50	NA
OC	NA	NA	NA	NA	NA	NA	NA	NA	100
EC	NA	NA	NA	NA	NA	NA	NA	NA	100

<sup>a</sup>Minimum detection limit is three times the standard deviation of the blank for a filter of 1 mg/cm<sup>2</sup> areal density.

ICP/AES = Inductively Coupled Plasma with Atomic Emission Spectroscopy.

AA = Atomic Absorption Spectrophotometry.

PIXE = Proton Induced X-ray Emissions Spectrometry.

XRF = Non-Dispersive X-ray Fluorescence Spectrometry.

INAA = Instrumental Neutron Activation Analysis.

IC = Ion Chromatography.

AC = Automated Colorimetry.

TOR = Thermal Optical Reflectance.

<sup>b</sup>Concentration is based on the extraction of 1/2 of a 47 mm quartz-fiber filter in 15 ml of deionized-distilled water, with a nominal flow rate of 20 L/min for 24-h samples.

<sup>c</sup>Concentration is based on 13.8 cm<sup>2</sup> deposit area for a 47 mm ringed teflon-membrane filter, with a nominal flow rate of 20 L/min for 24-h samples with 100 sec radiation time.

<sup>d</sup>Harman (1989).

<sup>e</sup>Fernandez de la Mora (1989).

<sup>f</sup>Olmez (1989).

<sup>g</sup>Eldred et al. (1993).

<sup>h</sup>Not Available.

### 4.3.1 Mass Measurement Methods

Particulate mass concentration is the most commonly made measurement on aerosol samples. It is used to determine compliance with PM<sub>10</sub> standards and to select certain samples for more detailed, and more expensive, chemical analyses. As noted in Section 2, the beta attenuation and inertial microbalance methods have been incorporated into in situ measurement systems which acquire real-time mass measurements. Gravimetric analysis is used almost exclusively to obtain mass measurements of filters in a laboratory environment. The U.S. Environmental Protection Agency (1976) has published detailed procedures for mass analyses associated with 20.32 cm × 25.40 cm fiber filters, but the guidance for other types of filters used for chemical analyses is less well documented.

Gravimetry measures the net mass on a filter by weighing the filter before and after sampling with a balance in a temperature- and relative humidity-controlled environment. PM<sub>10</sub> reference methods require that filters be equilibrated for 24 h at a constant (within ±5%) relative humidity between 20 and 40% and at a constant (within ±3 °C) temperature between 15 and 30 °C. These are intended to minimize the liquid water associated with soluble compounds and to minimize the loss of volatile species. Nominal values of 30% RH and 15 to 20 °C best conserve the particle deposits during sample weighing.

Balances used to weigh 20.32 cm × 25.40 cm filters from high volume PM<sub>10</sub> samples must have a sensitivity of at least 100 µg. Balances used for medium volume PM<sub>10</sub> samples should have a sensitivity of at least 10 µg, and those used for low-volume PM<sub>10</sub> samples should have a sensitivity of at least 1 µg. Modifications to the balance chamber are sometimes needed to accommodate filters of different sizes. All filters, even those from high-volume PM<sub>10</sub> samplers, should be handled with gloved hands when subsequent chemical analyses are a possibility.

Balance calibrations should be established before and after each weighing session using Class M and Class S standards, and they should be verified with a standard mass every 10 filters. Approximately one out of ten filters should be re-weighed by a different person at a later time. These re-weights should be used to calculate the precision of the measurement as outlined by Watson et al. (1989a).

Feeney et al. (1984) examined the gravimetric measurement of lightly loaded membrane filters and obtained excellent precision and accuracy. The sensitivity of the electrobalance is

about  $\pm 0.001$  mg, though tolerances on re-weights of Teflon-membrane filters are typically  $\pm 0.010$  mg. The main interference in gravimetric analysis of filters results from electrostatic effects. Engelbrecht et al. (1980) found that residual charge on a filter could produce an electrostatic interaction between the filter on the pan and the metal casing of the electrobalance. This charge can be removed by exposing the filter to a radioactive polonium source before and during sample weighing.

Beta attenuation methods have been applied in the laboratory as well as in the field, and the results are comparable to those of gravimetric measurements. The precision of beta-gauge measurements has been shown to be  $\pm 5 \mu\text{g}/\text{m}^3$  or better for counting intervals of one minute per sample, which translates into  $\pm 32 \mu\text{g}/\text{filter}$  for 37 mm diameter substrates. This is substantially higher than the  $\pm 6 \mu\text{g}/\text{filter}$  precision determined by gravimetric analysis using an electrobalance (Feeney et al., 1984). Jaklevic et al. (1981) found equivalent accuracy and precision for both techniques as they were used in that study. Courtney et al. (1982) found beta attenuation and gravimetric mass measurements to differ by less than  $\pm 5\%$ . Patashnick and Rupprecht (1991) examine results from TEOM samplers operated alongside filter-based  $\text{PM}_{10}$  samplers, and Shimp (1988) reports comparisons with beta attenuation field monitors; these comparisons all show good agreement for mass measurements.

#### **4.3.2 Physical Analysis**

The most common interest in elemental composition derives from concerns about health effects and the utility of these elements to trace the sources of suspended particles. Instrumental neutron activation analysis (INAA), photon-induced x-ray fluorescence (XRF), particle-induced x-ray emission (PIXE), atomic absorption spectrophotometry (AAS), inductively-coupled plasma with atomic emission spectroscopy (ICP/AES), and scanning electron microscopy with x-ray fluorescence (SEM/XRF) have all been applied to elemental measurements of aerosol samples. AAS and ICP/AES are also appropriate for ion measurements when the particles are extracted in deionized-distilled water (DDW). Since air filters contain very small particle deposits ( $20$  to  $100 \mu\text{g}/\text{cm}^2$ ), preference is given to methods that can accommodate small sample sizes. XRF and PIXE leave the sample intact after analysis so that it can be submitted to additional examinations by other methods. Excellent agreement was found for the



intercomparison of elements acquired from the XRF and PIXE analyses (Cahill, 1980). The analytical measurement specifications of air filter samples for the different elemental analysis is shown in Table 4-2.

#### **4.3.2.1 X-Ray Fluorescence of Trace Elements**

In x-ray fluorescence (XRF) (Dzubay and Stevens, 1975; Hammerle and Pierson, 1975; Jaklevic et al., 1977; Torok and Van Grieken, 1994), the filter deposit is irradiated by high energy x-rays that eject inner shell electrons from the atoms of each element in the sample. When a higher energy electron drops into the vacant lower energy orbital, a fluorescent x-ray photon is released. The energy of this photon is unique to each element, and the number of photons is proportional to the concentration of the element. Concentrations are quantified by comparing photon counts for a sample with those obtained from thin-film standards of known concentration.

XRF methods can be broadly divided into two categories: wavelength dispersive x-ray fluorescence (WDXRF), which utilizes crystal diffraction for observation of fluorescent x-rays, and energy dispersive x-ray fluorescence (EDXRF), which uses a silicon semiconductor detector. The WDXRF method is characterized by high spectral resolution, which minimizes peak overlaps. It requires high power excitation to overcome low sensitivity, resulting in excessive sample heating and potential degradation. Conversely, EDXRF features high sensitivity but less spectral resolution, requiring complex spectral deconvolution procedures.

XRF methods can be further categorized as direct/filtered excitation, where the x-ray beam from the tube is optionally filtered and then focused directly on the sample, or secondary target excitation, where the beam is focused on a target of material selected to produce x-rays of the desired energy. The secondary fluorescent radiation is then used to excite the samples. The direct/filtered approach has the advantage of delivering higher incident radiation flux to the sample for a given x-ray tube power, since about 99% of the incident energy is lost in a secondary fluorescence. However, the secondary fluorescence approach, produces a more nearly monochromatic excitation that reduces unwanted scatter from the filter, thereby yielding better detection limits.

XRF is usually performed on Teflon-membrane filters for a variety of trace elements. A typical XRF system is schematically illustrated in Figure 4-24. The x-ray output stability should

be within  $\pm 0.25\%$  for any 8-h period within a 24-h duration. Typically, analyses are controlled, spectra are acquired, and elemental concentrations are calculated by software on a computer that is interfaced to the analyzer. Separate XRF analyses are conducted on each sample to optimize detection limits for the specified elements. A comparison of the minimum detectable limits of Teflon-membrane and quartz-fiber filters is listed in Table 4-3. Figure 4-25 shows an example of an XRF spectrum.

Three types of XRF standards are used for calibration, performance testing, and auditing: (1) vacuum-deposited thin-film elements and compounds (Micromatter); (2) polymer films (Dzubay et al., 1981); and (3) National Institute of Science and Technology (NIST, formerly NBS) thin-glass films. The thin film standards cover the largest number of elements and are used to establish calibration curves, while the polymer film standards are used to verify the accuracy of the thin film standards. The NIST standards are used to validate the accuracy of the calibration curves. NIST produces the definitive standard reference materials, but these are only available for the species of aluminum, silicon, calcium, iron, cobalt, copper, manganese, and uranium (SRM 1832), and silicon, potassium, titanium, iron, zinc, and lead (SRM 1833). One or more separate Micromatter thin-film standards are used to calibrate the system for each element.

Sensitivity factors (number of x-ray counts per  $\mu\text{g}/\text{cm}^2$  of the element) are determined for each excitation condition. These factors are then adjusted for absorption of the incident and emitted radiation in the thin film. These sensitivity factors are plotted as a function of atomic number and a smooth curve is fitted to the experimental values. The calibration sensitivities are then read from these curves for the atomic numbers of each element in each excitation condition. NIST standards are analyzed on a periodic basis to verify the sensitivity factors. A multi-layer thin film standard prepared by Micromatter is analyzed with each set of samples to check the stability of the instrument response. When deviations from specified values are greater than  $\pm 5\%$ , the system should be re-calibrated.

The sensitivity factors are multiplied by the net peak intensities yielded by ambient samples to obtain the  $\mu\text{g}/\text{cm}^2$  deposit for each element. The net peak intensity is obtained

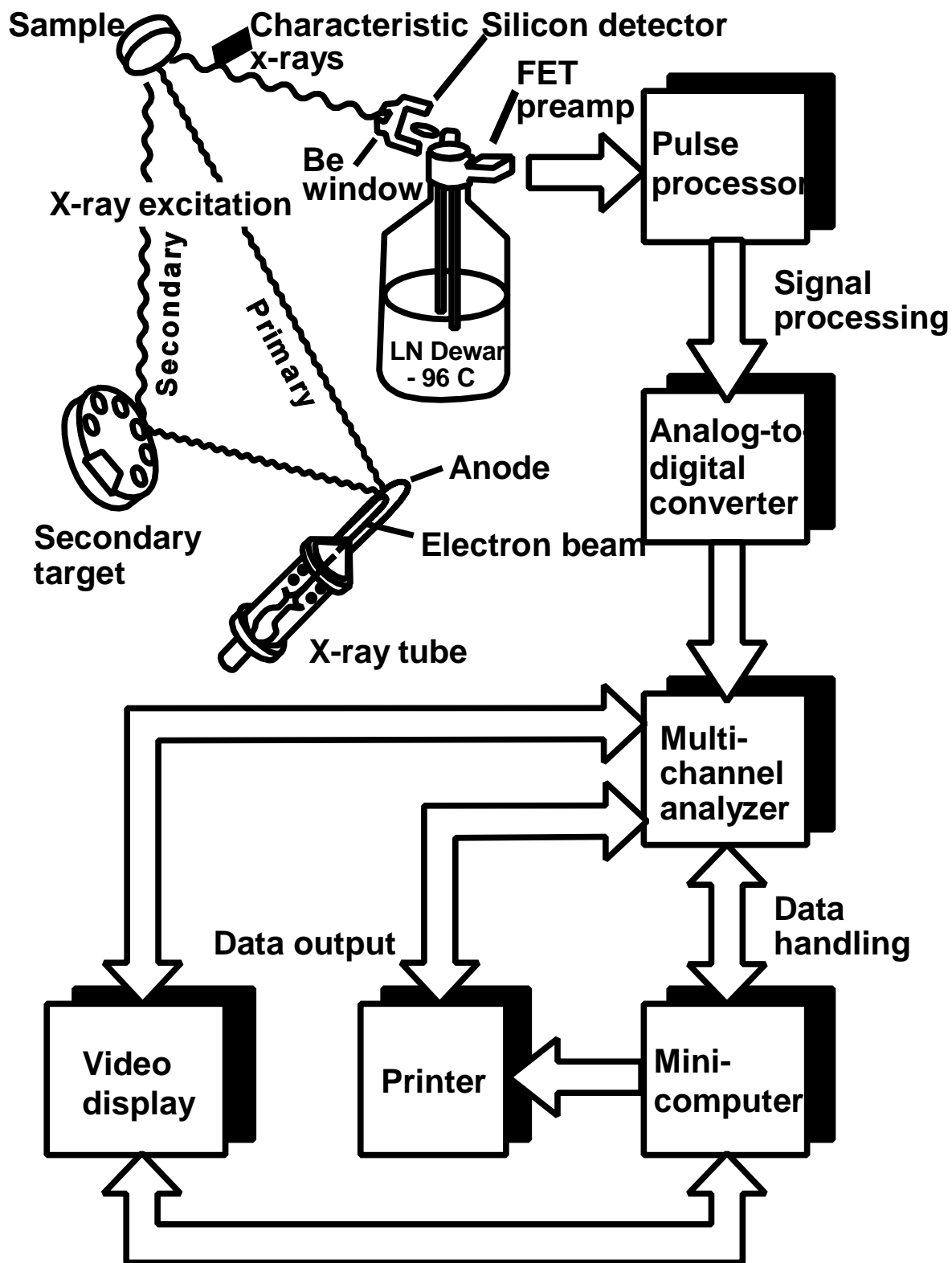


Figure 4-24. Schematic of a typical X-ray fluorescence system.

**TABLE 4-3. MINIMUM DETECTABLE LIMITS<sup>a</sup> FOR X-RAY FLUORESCENCE  
ANALYSIS OF AIR FILTERS**

Element	Condition Number <sup>d</sup>	Quartz-Fiber Filter <sup>b</sup>	Teflon Membrane Filter <sup>c</sup>			
		Protocol QA- A ng/cm <sup>2</sup> <sup>e</sup>	Protocol A ng/cm <sup>2</sup> <sup>d</sup>	Protocol B ng/cm <sup>2</sup>	Protocol C ng/cm <sup>2</sup>	Protocol D ng/cm <sup>2</sup>
Al	5	NA <sup>f</sup>	10	7.2	3.6	2.5
Si	5	NA	6.3	4.4	2.2	1.4
P	5	NA	5.6	4.0	2.0	1.4
S	5	40 <sup>g</sup>	5.0	3.5	1.8	1.2
Cl	4	30	10	7.4	3.7	2.6
K	4	40	6.1	4.3	2.2	1.5
Ca	4	100	4.5	3.2	1.6	1.1
Ti	3	50	2.9	2.1	1.0	0.73
V	3	20	2.5	1.7	0.87	0.62
Cr	3	8	1.9	1.4	0.67	0.48
Mn	3	7	1.6	1.1	0.56	0.40
Fe	3	15	1.5	1.1	0.54	0.38
Co	3	5	0.88	0.62	0.31	0.22
Ni	3	4	0.89	0.63	0.31	0.22
Cu	3	4	1.1	0.76	0.38	0.27
Zn	3	6	1.1	0.76	0.38	0.27
Ga	2	8	1.9	1.4	0.68	0.48
As	2	9	1.6	1.1	0.56	0.39
Se	2	5	1.2	0.86	0.43	0.31
Br	2	5	1.0	0.72	0.36	0.25
Rb	2	5	1.0	0.68	0.34	0.24
Sr	2	8	1.1	0.78	0.39	0.28
Y	2	8	1.3	0.92	0.46	0.33
Zr	2	10	1.7	1.2	0.59	0.42
Mo	4	20	2.7	1.9	0.95	0.67
Pd	1	20	11	7.6	3.8	2.7
Ag	1	20	12	8.6	4.3	3.0
Cd	1	25	12	8.6	4.3	3.0
In	1	30	13	9.5	4.8	3.4

**TABLE 4-3 (cont'd). MINIMUM DETECTABLE LIMITS<sup>a</sup> FOR X-RAY  
FLUORESCENCE ANALYSIS OF AIR FILTERS**

Element	Condition Number <sup>d</sup>	Quartz-Fiber Filter <sup>b</sup>	Teflon Membrane Filter <sup>c</sup>			
		Protocol QA-A ng/cm <sup>2</sup> <sup>e</sup>	Protocol A ng/cm <sup>2</sup> <sup>d</sup>	Protocol B ng/cm <sup>2</sup>	Protocol C ng/cm <sup>2</sup>	Protocol D ng/cm <sup>2</sup>
Sn	1	40	17	12	6.2	4.4
Sb	1	50	18	13	6.4	4.5
Ba	1	170	52	37	18	13
La	1	190	62	44	22	16
Au	2	NA	3.1	2.2	1.1	0.77
Hg	2	20	2.6	1.8	0.91	0.65
Tl	2	NA	2.5	1.8	0.88	0.62
Pb	2	14	3.0	2.2	1.1	0.76
U	2	NA	2.3	1.7	0.83	0.59

<sup>a</sup>MDL defined as three times the standard deviation of the blank for a filter of 1 mg/cm<sup>2</sup> areal density.

<sup>b</sup>Analysis times are 100 sec. for Conditions 1 and 4, and 400 sec. for Conditions 2 and 3. Actual MDL's for quartz filters vary from batch to batch due to elemental contamination variability.

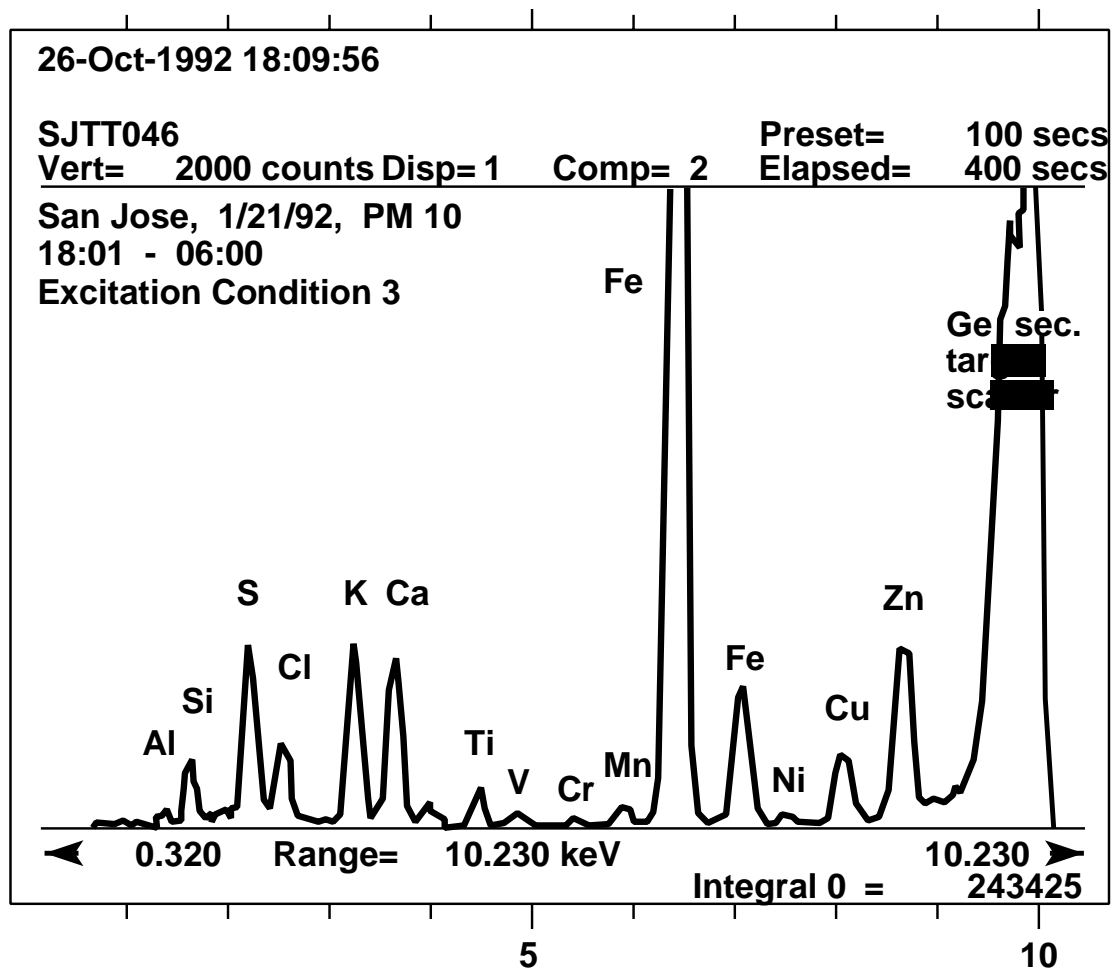
<sup>c</sup>Standard protocol, developed at the Desert Research Institute, University and Community College System of Nevada, Reno, NV, analysis times are 100 sec. for Conditions 1, 4 and 5, and 400 sec. for Conditions 2 and 3 for Protocol A; 200 sec. for Conditions 1, 4 and 5 and 800 sec. for Conditions 2 and 3 for Protocol B; 800 sec. for Conditions 1, 4 and 5 and 3,200 sec. for Conditions 2 and 3 for Protocol C; and 1600 sec. for Conditions 1, 4 and 5 and 6400 sec. for Conditions 2 and 3 for Protocol D.

<sup>d</sup>Condition 1 is direct mode excitation with a primary excitation filter of 0.15 mm thick Mo. Tube voltage is 50 KV and tube current is 0.6 mA. Condition 2 is direct mode excitation with a primary excitation filter of 0.13 mm thick Rh. Tube voltage is 35 KV and tube voltage is 2.0 mA. Condition 3 uses Ge secondary target excitation with the secondary excitation filtered by a Whatman 41 filter. Tube voltage is 30 KV and tube current is 3.3 mA. Condition 4 uses Ti secondary target excitation with the secondary excitation filtered by 3.8  $\mu$ m thick mylar film. Tube voltage is 30 KV and tube current is 3.3 mA. Condition 5 uses direct mode excitation with a primary excitation filter consisting of 3 layers of Whatman 41 filters. Tube voltage is 8 KV and tube current os 0.6 mA. Multi-channel analyzer energy range is 0 to 40 KeV for condition 1, 0 - 20 KeV for condition 2, and 0 to 10 KeV for conditions 3, 4, and 5.

<sup>e</sup>Typical exposed area is 406 cm<sup>2</sup> for standard high-volume filters; 6.4 cm<sup>2</sup> for 37 mm ringed Teflon-membrane filters; and 13.8 cm<sup>2</sup> for 47 mm ringed Teflon-membrane filters.

<sup>f</sup>Information not available.

<sup>g</sup>For condition 4.



**Figure 4-25. Example of an X-ray fluorescence spectrum.**

Source: Chow and Watson (1994).

by: (1) subtracting background radiation; (2) subtracting spectral interferences; and (3) adjusting for x-ray absorption.

XRF analysis of air particulate samples has had widest application to samples collected on membrane-type filters such as Teflon- or polycarbonate-membrane filter substrates. These membrane filters collect the deposit on their surfaces, which eliminates biases due to absorption of x-rays by the filter material. These filters also have a low areal density which minimizes the scatter of incident x-rays, and their inherent trace element content is very low. Quartz-fiber filters used for high-volume aerosol sampling do not exhibit these features. As noted earlier, blank elemental concentrations in quartz-fiber filters that have not undergone acceptance testing can be several orders of magnitude higher than the concentrations in the particulate deposits.

The concentrations vary substantially among the different types of quartz-fiber filters and even within the same filter type and manufacturing lot. Blank impurity concentrations and their variabilities decrease the precision of background subtraction from the XRF spectral data, resulting in higher detection limits. Impurities observed in various types of glass- and quartz-fiber filters include aluminum, silicon, sulfur, chlorine, potassium, calcium, iron, nickel, copper, zinc, rubidium, strontium, molybdenum, barium, and lead. Concentrations for aluminum, silicon, phosphorus, sulfur, and chlorine cannot be determined for quartz-fiber filters because of the large silicon content of the filters.

Quartz-fiber filters also trap particles within the filter matrix, rather than on the surface. This causes absorption of X rays within the filter fibers yielding lower concentrations than would otherwise be measured. The magnitude of this absorption increases exponentially as the atomic number of the measured element decreases and varies from sample to sample. Absorption factors generally are "1.2" or less for iron and heavier elements, but can be from "2" to "5" for sulfur.

Quartz-fiber filters are much thicker than membrane filters resulting in an increased scattering of x-rays and a consequent increase in background and degradation of detection limits. The increased x-ray scatter also overloads the x-ray detector which requires samples to be analyzed at a lowered x-ray intensity. These effects alone can result in degradation of detection limits by up to a factor of 10 with respect to Teflon-membrane substrates.

Larger particles collected during aerosol sampling have sufficient size to cause absorption of x-rays within the particles. Attenuation factors for fine particles ( $PM_{2.5}$ , particles with aerodynamic diameters equal to or less than  $2.5 \mu m$ ) are generally negligible (Criss, 1976), even for the lightest elements, but these attenuations can be significant for coarse fraction particles (particles with aerodynamic diameters from  $2.5$  to  $10 \mu m$ ). Correction factors for XRF have been derived using the theory of Dzubay and Nelson (1975) and should be applied to coarse particle measurements.

#### **4.3.2.2 Particle Induced X-Ray Emission of Trace Elements**

Particle Induced X-Ray Emission (PIXE) is another form of elemental analysis based on the characteristics of x-rays and the nature of x-ray detection (Cahill et al., 1987; 1989). PIXE uses beams of energetic ions, consisting of protons at an energy level of 2 to 5 MeV, to create

inner electron shell vacancies. As inner electron shell atomic vacancies are filled by outer electrons, the emitted characteristics of x-rays can be detected by wavelength dispersion (which is scattering from a crystal) or by energy dispersion (which involves direct conversion of x-rays). The development of focusing energetic proton beams (proton microprobes) has expanded the application of PIXE from environmental and biological sciences to geology and material sciences. Figure 4-26 illustrates a typical PIXE setup in a thin target mode (Cahill, et al., 1989). PIXE analysis is often used for impactor samples or small filter substrates, since proton beams can be focused to a small area with no loss of sensitivity (Cahill and Wakabayashi, 1993).

Very thick filters or thick particle deposits on filter substrates scatter the excitation protons and lower the signal-to-noise ratio for PIXE. X-ray analysis methods, such as PIXE and XRF, require particle size diameter corrections (for low atomic number targets) associated with a spherical particle of a given diameter (typically particles with aerodynamic diameters  $>2.5 \mu\text{m}$ ) and compositions typical in ambient aerosol studies. These analyses also require correction for sample loadings that reflect the passage of x-rays through a uniform deposit layer. Procedures for instrument calibration, spectrum process, and quality assurance are similar to those documented in Section 4.3.1.2 for XRF.

PIXE analysis can provide information on one of the widest range of elements in a single analysis, since x-ray results require two or three separate anodes. However, attempts to improve sensitivity of PIXE analysis may result in damage to Teflon-membrane filters. Recent developments (Malm et al., 1994) using PIXE analysis at moderate sensitivity plus single anode XRF analysis at high sensitivity for transition/heavy metals have achieved the minimum detectable limits of less than  $0.01 \text{ ng/m}^3$ . With the addition of hydrogen analysis (a surrogate for organic matter), almost all gravimetric mass concentrations can be explained (Cahill, et al., 1987).

XRF and PIXE are the most commonly used elemental analysis methods owing to their nondestructive multi-element capabilities, relatively low cost, high detection limits, and preservation of the filter for additional analyses. XRF sometimes needs to be supplemented with INAA when extremely low detection limits are needed, but the high cost of INAA precludes this method from being applied to large numbers of samples. AAS is a good



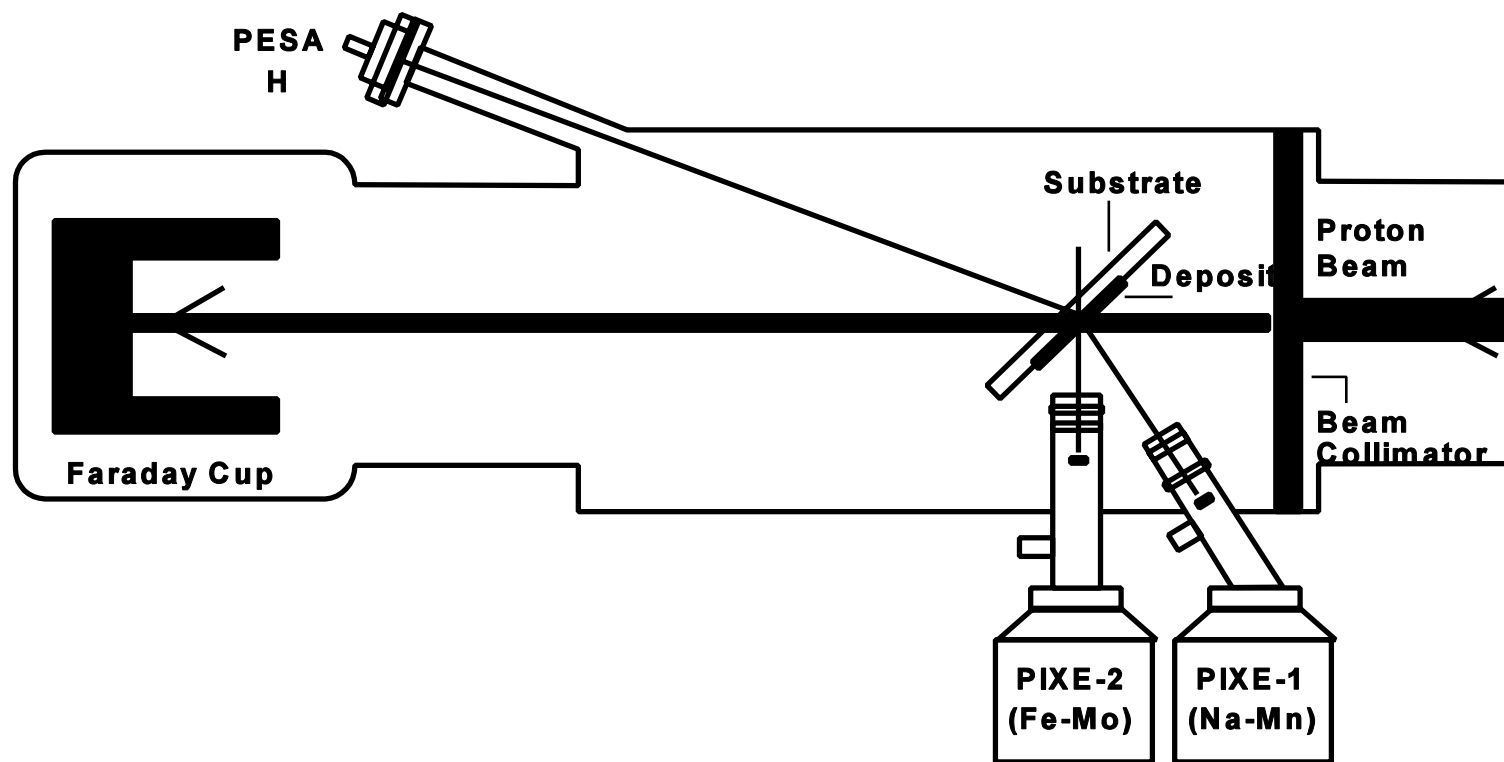


Figure 4-26. Schematic of a PIXE/PESA analysis system.

alternative for water-soluble species, especially for low atomic number. ICP/AES analysis is a viable alternative, but it is less desirable because of the sample extraction elements such as sodium and magnesium, but it requires large dilution factors to measure many different elements expense and the destruction of the filter.

#### **4.3.2.3 Instrumental Neutron Activation Analysis of Trace Elements**

Instrumental neutron activation analysis (INAA) (Dams et al., 1970; Zoller and Gordon, 1970; Olmez, 1989; Ondov and Divita, 1993) basically involves irradiation of a thin membrane filter sample in the core of a nuclear reactor for periods ranging from a few minutes to several hours. Bombardment of the sample with neutrons induces a nuclear reaction of the stable isotopes in the sample. The energies of the gamma rays emitted by the decay of this induced radioactivity are used to identify them, and therefore, their parents. With the use of prepared elemental standards, the amount of parent element in the sample can be determined since the intensity of these gamma rays are proportional to their number.

The gamma-ray spectra of radioactive species are usually collected with a high resolution germanium detector utilizing commercially available amplifiers and multi-channel analyzers. Typical detector efficiencies range from 10 to 40% relative to a 3 × 3 in. sodium iodide detector. Detector system resolution, measured as the full-width at half-maximum for Table 4-4, the 1,332 KeV gamma-ray peak of <sup>60</sup>Co, should be less than 2.3 KeV in order to provide adequate resolution between isotopes of neighboring energies.

In order to obtain a full suite of elemental analysis results (often over 40 elements), multiple counting periods and irradiations are performed on the same sample (e.g., two irradiations would produce elements separated into short- and long-lived decay products). An example of the elements determined from multiple irradiations and counting periods and the irradiation, cooling, and counting times used for ambient particulate samples collected on Teflon-membrane filter material are summarized in Table 4-4 (Divita, 1993). These irradiations were performed at the 20-MW NIST Research Reactor operated at 15-MW (neutron flux of  $7.7 \times 10^{13}$  and  $2.7 \times 10^{13}$  neutron/cm<sup>2</sup> × s).

The power of INAA is that it is not generally subject to interferences like XRF or PIXE due to a much better ratio of gamma ray peak widths to total spectral width, by a factor of about 20. INAA does not quantify some of the abundant species in ambient

**TABLE 4-4. INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS COUNTING  
SCHEME AND ELEMENTS MEASURED**

Counting Period	Irradiation Time	Cooling Time	Counting Time	Elements Measured
Short-Lived 1	10 min	5 min	5 min	Mg, Al, S, Ca, Ti, V, Cu
Short-Lived 2		20 min	20 min	Na, Mg, Cl, K, Ca, Mn, Zn, Ga, Br, Sr, In, I, Ba
Long-Lived 1	4-6 h	3-4 days	6-8 h	Na, K, Ga, As, Br, Mo, Cd, Sb, La, Nd, Sn, Yb, Lu, W, Au, U
Long-Lived 2		30 days	12-24 h	Sc, Cr, Fe, Co, Zn, Se, Sr, Ag, Sb, Cs, Ba, Ce, Nd, Eu, Gd, Tb, Lu, Hf, Ta, Th

particulate matter such as silicon, nickel, tin, cadmin, mercury, and lead. While INAA is technically nondestructive, sample preparation involves folding the samples tightly and sealing it in plastic, and the irradiation process makes the filter membrane brittle and radioactive. These factors limit the use of the sample for subsequent analyses by other methods. The technique also suffers from the fact that a nuclear reactor is usually used as a source of neutrons. However, since the advent of high-resolution gamma-ray detectors, individual samples can be analyzed for numerous elements simultaneously, most at remarkably trace levels without the need for chemical separation. This greatly diminishes the danger of contamination due to excessive sample handling and introduction of chemical reagents used for separation procedures.

#### **4.3.2.4 Microscopy Analysis of Particle Size, Shape, and Composition**

Morphological and chemical features of particles can be used to identify the sources and transport mechanism of airborne particles. The chemical analysis of individual particles allows the attribution of specific pollution sources more straightforward while the abundance of a specific group is a representative of the source strength. Both light (optical) and scanning electron microscopy have been applied in environmental studies to examine the

single particles (e.g., Casuccio et al., 1983; Bruynseels et al., 1988; Van Borm and Adams, 1988; Van Borm et al., 1989; Cornille et al., 1990; Hopke and Casuccio, 1991; Turpin et al., 1993a).

Light microscopy has been used for providing particle size information regarding the morphology of microscopic features (Crutcher, 1982). The practical resolution of optical microscopes is limited by the wavelengths associated with light of the visible spectrum. When features of interest occur in micron and submicron size ranges, detailed resolution cannot be obtained. The practical resolution of light microscopy is typically 1 to 2  $\mu\text{m}$  (Meyer-Arendt, 1972).

The use of accelerated electrons in electron microscopy (a) allows for the formation of magnified images and an increased depth of field and (b) provides the resolution of a few angstroms ( $10^{-4}$   $\mu\text{m}$ ). Electron microscopy has now evolved to include: (1) the transmission electron microscope (TEM); (2) the scanning electron microscope (SEM), and; (3) the scanning transmission electron microscope (STEM) (Hearle et al. 1972; Lee et al., 1979; Lee and Fisher, 1980; Lee and Kelly, 1980; Lee et al., 1981; Johnson et al., 1981; McIntyre and Johnson, 1982; Casuccio et al., 1983; Wernisch, 1985, 1986; Kim et al., 1987; Kim and Hopke, 1988; Dzubay and Mamane, 1989; Schamber, 1993).

The SEM and STEM use accelerated electrons to strike the sample. As the electron beam strikes the samples, various signals (e.g., secondary, backscattered, and Auger electrons, characteristic x-rays, photons, and cathodoluminescence) are generated. These signals can be collected to provide highly detailed information on a point-by-point basis. The secondary electron signal yields a sample image with three-dimensional perspective, high depth of field, and illuminated appearance. Back scattered electron images are used to separate phases containing elements of different atomic number.

The information obtained from light and scanning microscopy analyses are usually considered to be qualitative, due to the limited number of particles counted. To achieve a quantitative analysis, a sufficient number of particles must be properly sized and identified by morphology and/or chemistry to represent the entire sample. The selection of filter media, optimal particle loadings, and sample handling methods are also of importance. In this manner, the microscopic characteristics can be directly and reliably related to the bulk or macroscopic properties of the sample (Casuccio et al., 1983).

Microscopic analysis requires a high degree of skill and extensive quality assurance to provide quantitative information. The techniques is complex and expensive when quantitative analysis is required. The evolution of computer technology has allowed for quantitative analysis of particle samples of an entire population of features. With advanced pattern recognition methods, data from individual particle features can be sorted and summarized by size and composition, permitting improved quantitative source apportionment (Bruynseels et al., 1988; Hopke and Casuccio, 1991). Casuccio et al. (1983) summarized the pros and cons of automatic scanning electron microscopy.

Recent development of the SEM/XRF allows analysis of elemental compositions and morphological information on small quantities of material (Bruynseels et al., 1988). Coupled with statistical data analysis, computer controlled scanning electron microscopy shows great promise for identifying and quantifying complex pollution sources in the field of receptor modeling source apportionment (e.g., Griffin and Goldberg, 1979; Janocko et al., 1982; Johnson et al., 1982; Massart and Kaufman, 1983; Hopke, 1985; Derde et al., 1987, Saucy et al., 1987; Mamane, 1988; Dzubay and Mamane, 1989).

#### **4.3.3 Wet Chemical Analysis**

Aerosol ions refer to chemical compounds that are soluble in water. The water-soluble portion of suspended particles associates itself with liquid water in the atmosphere when relative humidity increases, thereby changing the light scattering properties of these particles. Different emissions sources may also be distinguished by their soluble and non-soluble fractions. Gaseous precursors can also be converted to their ionic counterparts when they interact with chemicals impregnated on the filter material.

Several simple ions, such as soluble sodium, magnesium, potassium, and calcium are best quantified by atomic absorption spectrometry (AAS) as described above. In practice, AAS has been very useful for measuring water-soluble potassium and sodium, which are important in apportioning sources of vegetative burning and sea salt, respectively. Polyatomic ions such as sulfate, nitrate, ammonium, and phosphate must be quantified by other methods such as ion chromatography (IC) and automated colorimetry (AC). Simple ions, such as chloride, chromium III, and chromium IV, may also be measured by these methods along with the polyatomic ions.

All ion analysis methods require filters to be extracted in DDW and then filtered to remove the insoluble residue. The extraction volume needs to be as small as possible, lest the solution become too dilute to detect the desired constituents. Each square centimeter of filter should be extracted in no more than 2 ml of solvent for typical sampler flow rates of 20 to 30 L/min and sample durations of 24 h. This often results in no more than 20 ml of extract that can be submitted to the different analytical methods, thereby giving preference to those methods which require only a small sample volume. Sufficient sample deposit must be acquired to account for the dilution volume required by each method.

When other analyses are to be performed on the same filter, the filter must first be sectioned using a precision positioning jig attached to a paper cutter. For rectangular filters (typically 20.32 cm by 25.40 cm), a 2.0 cm by 20.32 cm wide strip is cut from the center two-thirds of the filter. Circular filters of 25-, 37-, and 47-mm diameters are usually cut in half for these analyses, so the results need to be multiplied by two to obtain the deposit on the entire filter. Filter materials that can be easily sectioned without damage to the filter or the deposit must be chosen for these analyses.

#### **4.3.3.1 Ion Chromatographic Analysis for Chloride, Nitrate, and Sulfate**

Ion chromatography (IC) can be used for both anions (fluoride  $[F^-]$ , chloride  $[Cl^-]$ , nitrite  $[NO_2^-]$ , bromide  $[Br^-]$ , nitrate  $[NO_3^-]$ , phosphate  $[PO_4^{3-}]$ , sulfate  $[SO_4^{2-}]$ ) and cations (soluble potassium  $[K^+]$ , ammonium  $[NH_4^+]$ , soluble sodium  $[Na^+]$ ) with separate columns. Applied to aerosol samples, the anions are most commonly analyzed by IC with the cations being analyzed by a combination of atomic absorption spectrophotometry (AAS) and automated colorimetry (AC) (U.S. EPA, 1994). In IC (Small et al., 1975; Mulik et al., 1976; Butler et al., 1978) the sample extract passes through an ion-exchange column that separates the ions in time for individual quantification, usually by a electroconductivity detector. Figure 4-27 shows a schematic representation of the IC system. Prior to detection, the column effluent enters a suppressor column where the chemical composition of the eluent is altered, resulting in a lower background conductivity. The ions are identified by their elution/retention times and are quantified by the conductivity peak area or peak height. IC is especially desirable for particle samples because it provides results for several ions with a single analysis and it uses a small portion of the filter extract with low detection limits.

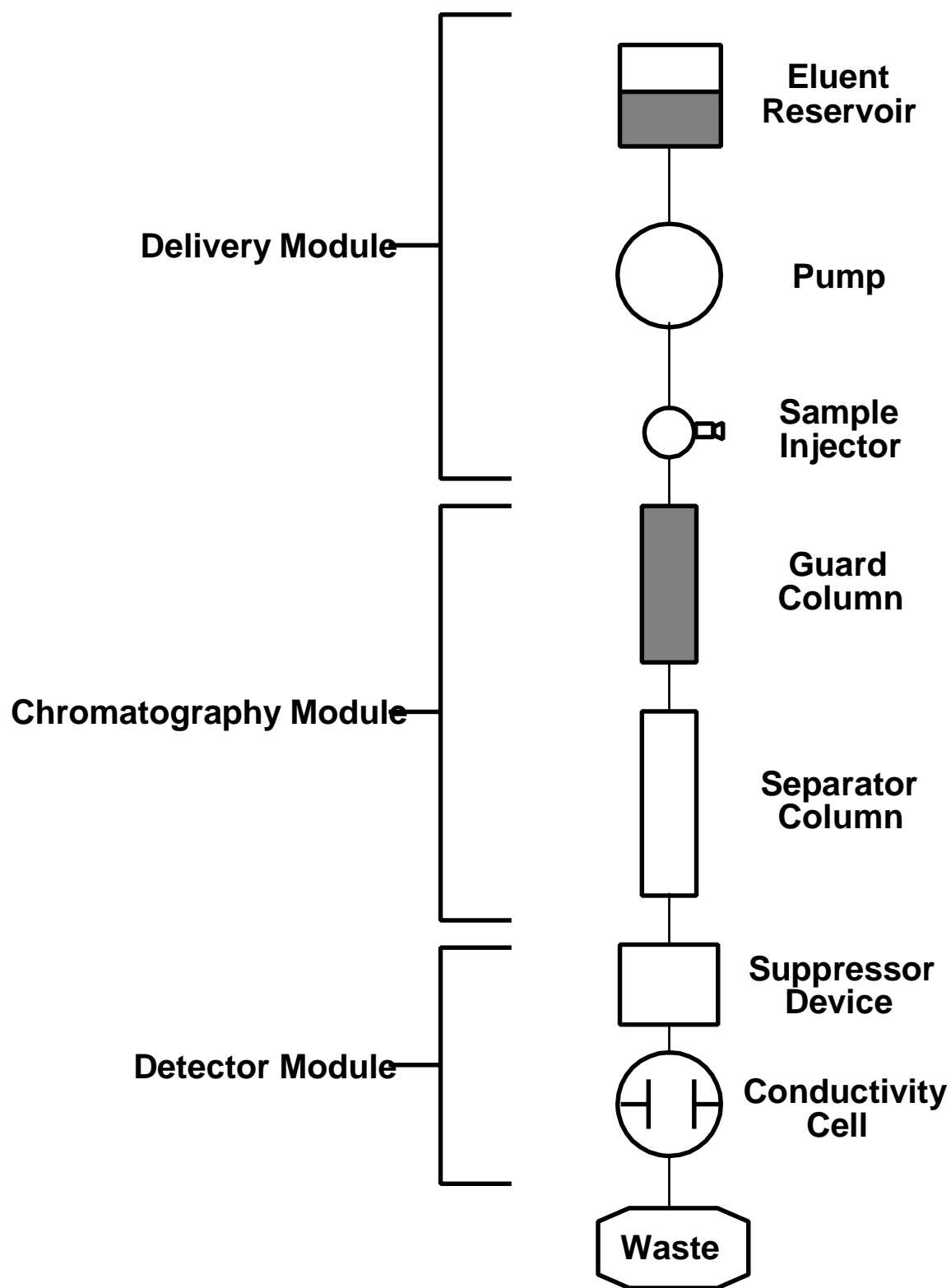
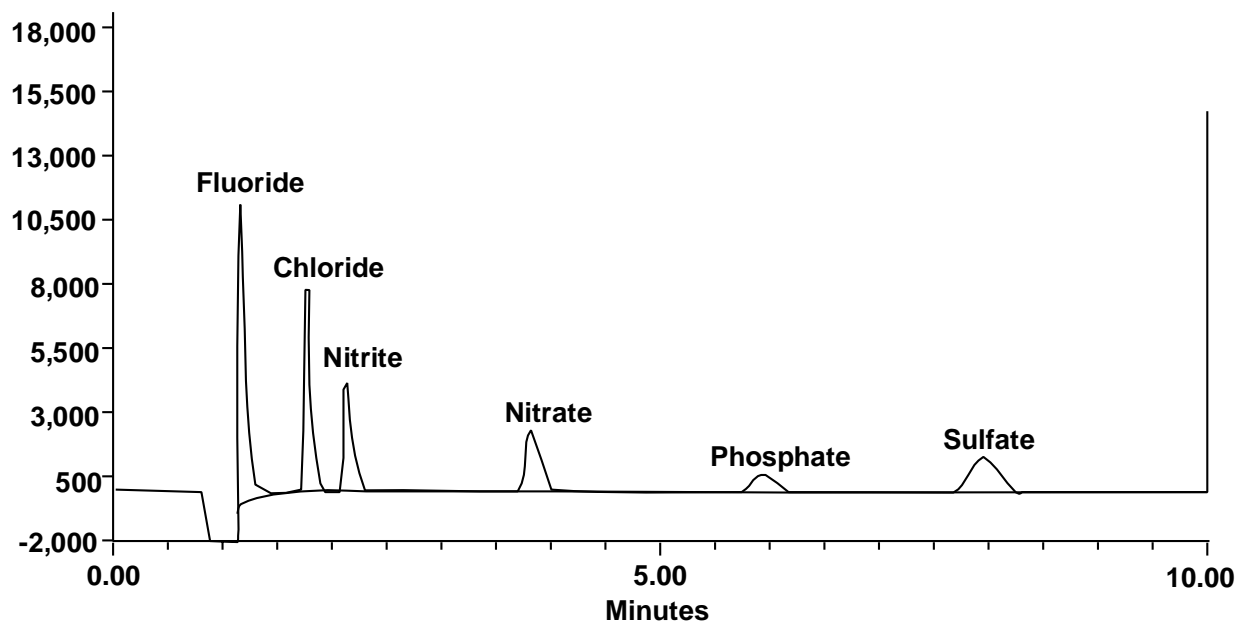


Figure 4-27. Schematic representation of an ion chromatography system.

Water-soluble chloride ( $\text{Cl}^-$ ), nitrate ( $\text{NO}_3^-$ ), and sulfate ( $\text{SO}_4^{2-}$ ) are the most commonly measured anions in aerosol samples. Figure 4-28 shows an example of an IC anion chromatogram. IC analyses can be automated by interfacing to an automatic sampler that can conduct unattended analysis of as many as 400 samples (Tejada et al., 1978).



**Figure 4-28. Example of an ion chromatogram showing the separation of fluoride, chloride, nitrite, nitrate, phosphate, and sulfate ions.**

Several independent quality assurance (QA) standards should be used to check the calibration curve. The standards that are traceable to NIST simulated rainwater standards are: Environmental Resource Associates (ERA, Arvada, CA) custom standards containing the anions measured at a concentration of  $100\ \mu\text{g}/\text{ml}$ , ERA Waste Water Nutrient Standard, ERA Waste Water Mineral Standard, and Alltech individual standards at  $200\ \mu\text{g}/\text{ml}$ . The QA standards are diluted in DDW to concentrations that are within the range of the calibration curve.

Calibration curves are performed weekly. Chemical compounds are identified by matching the retention time of each peak in the unknown sample with the retention times of



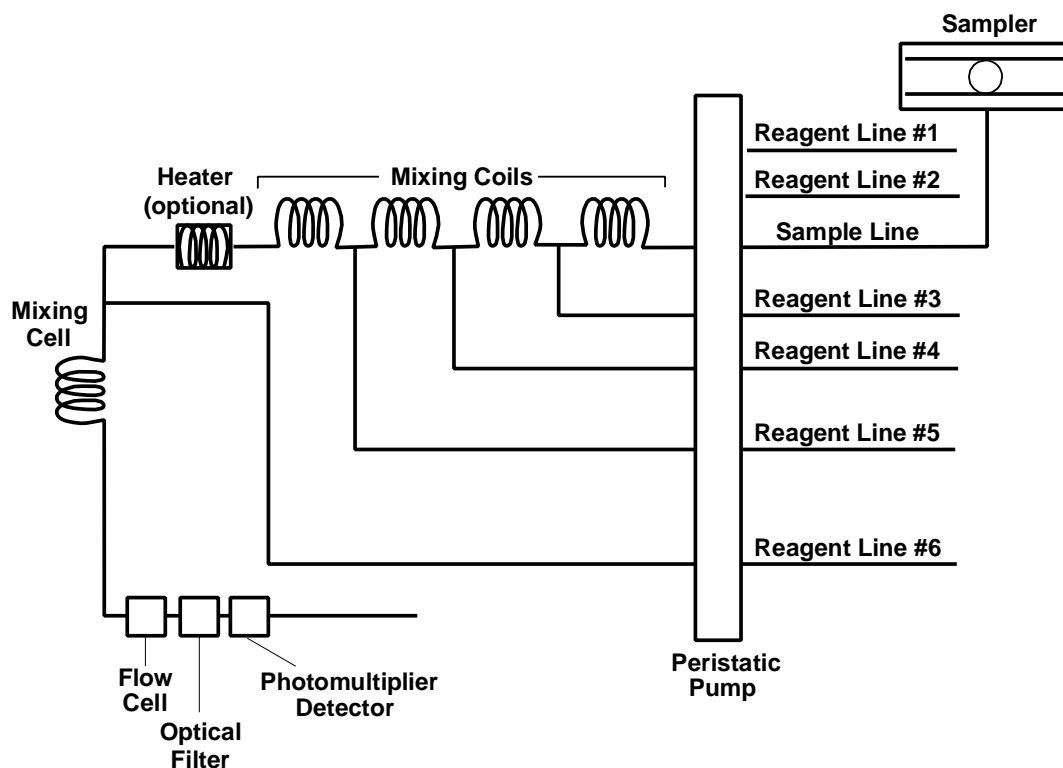
peaks in the chromatograms of the standards. The QA standards are analyzed at the beginning of each sample run to check calibrations. A DDW blank is analyzed after every 20 samples and a calibrations standard is analyzed after every 10 samples. These quality control (QC) checks verify the baseline and calibration respectively.

#### **4.3.3.2 Automated Colorimetric Analysis for Ammonium, Nitrate, and Sulfate**

Automated Colorimetry (AC) applies different colorimetric analyses to small sample volumes with automatic sample throughput. The most common ions measured are ammonium, chloride, nitrate, and sulfate (Butler et al., 1978; Fung et al., 1979). Since IC provides multi-species analysis for the anions, ammonium is most commonly measured by AC.

The AC system is illustrated schematically in Figure 4-29. The heart of the automated colorimetric system is a peristaltic pump, which introduces air bubbles into the sample stream at known intervals. These bubbles separate samples in the continuous stream. Each sample is mixed with reagents and subjected to appropriate reaction periods before submission to a colorimeter. The ion being measured usually reacts to form a colored liquid. The liquid absorbance is related to the amount of the ion in the sample by Beer's Law. This absorbance is measured by a photomultiplier tube through an interference filter specific to the species being measured.

The standard AC technique can analyze  $\approx 60$  samples per hour per channel, with minimal operator attention and relatively low maintenance and material costs. Several channels can be set up to simultaneously analyze several ions. The methylthymol-blue (MTB) method is applied to analyze sulfate. The reaction of sulfate with MTB-barium complex results in free ligand, which is measured colorimetrically at 460 nm. Nitrate is reduced to nitrite that reacts with sulfanilamide to form a diazo compound. This compound is then reacted to an azo dye for colorimetric determination at 520 nm. Ammonium is measured with the indophenol method. The sample is mixed sequentially with potassium sodium tartrate, sodium phenolate, sodium hypochlorite, sodium hydroxide, and sodium nitroprusside. The reaction results in a blue-colored solution with an absorbance measured at 630 nm. The system determines carry-over by analysis of a low concentration standard



**Figure 4-29. Schematic of a typical automated colorimetric system.**

following a high concentration. The percent carry-over is then automatically calculated and can be applied to the samples analyzed during the run.

Intercomparison studies between AC and IC have been conducted by Butler et al. (1978) and Fung et al. (1979). Butler et al. (1978) found excellent agreement between sulfate and nitrate measurements by AC and IC. The accuracy of both methods is within the experimental errors, with higher blank values observed for AC techniques. Comparable results were also obtained between the two methods by Fung et al. (1979). The choice between the two methods for sample analysis is dictated by sensitivity, scheduling, and cost constraints.

Two milliliters of extract in sample vials are placed in an autosampler that is controlled by a computer. Five standard concentrations (e.g.,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{NaNO}_3$ ) are prepared from American Chemical Society reagent-grade chemicals following the same procedure as that for IC standards. Each set of samples consists of two DDW blanks to establish a baseline, five calibration standards and a blank, then sets of ten samples followed by analysis of one of the standards and a replicate from a previous batch. The computer control allows additional analysis

of any filter extract to be repeated without the necessity of loading the extract into more than one vial.

#### **4.3.3.3 Atomic Absorption Spectrophotometric (AAS) and Inductive Coupled Plasma Atomic Emission Spectro (ICP/AES) Photometry Analyses for Trace Elements**

In atomic absorption spectrophotometric (AAS) analysis (Fernandez de la Mora, 1989), the sample is first extracted in a strong solvent to dissolve the solid material; the filter or a portion thereof is also dissolved during this process. A few milliliters of this extract are introduced into a flame where the elements are vaporized. Most elements absorb light at certain wavelengths in the visible spectrum, and a light beam with wavelengths specific to the elements being measured is directed through the flame to be detected by a monochromator. The light absorbed by the flame containing the extract is compared with the absorption from known standards to quantify the elemental concentrations. AAS requires an individual analysis for each element, and a large filter or several filters are needed to obtain concentrations for a large number of the elements specified in Table 4-3. AAS is a useful complement to other methods, such as XRF and PIXE, for species such as beryllium, sodium, and magnesium that are not well-quantified by XRF and PIXE. Airborne particles are chemically complex and do not dissolve easily into complete solution, regardless of the strength of the solvent. There is always a possibility that insoluble residues are left behind and soluble species may co-precipitate on them or on container walls.

In inductive coupled plasma atomic emission spectrophotometric (ICP/AES), (Lynch et al., 1980; Harman, 1989), the dissolved sample is introduced into an atmosphere of argon gas seeded with free electrons induced by high voltage from a surrounding Tesla coil. The high temperatures in the induced plasma raise valence electrons above their normally stable states. When these electrons return to their stable states, a photon of light is emitted which is unique to the element which was excited. This light is detected at specified wavelengths to identify the elements in the sample. ICP/AES acquires a large number of elemental concentrations using small sample volumes with acceptable detection limits for atmospheric samples. As with AAS, this method requires complete extraction and destruction of the sample.

### **4.3.4 Organic Analysis**

#### **4.3.4.1 Analysis of Organic Compounds**

Organic compounds comprise a major portion of airborne particles in the atmosphere, thus contributing to visibility degradation, and affecting the properties of clouds into which these particles are scavenged. Specific groups of organic compounds (e.g., polycyclic aromatic hydrocarbons, PAHs) have also been implicated in human health effects. However, due to the very complex composition of the organic fraction of atmospheric aerosols, the detailed composition and atmospheric distributions of organic aerosol constituents are still not well understood.

Sampling techniques for atmospheric particulate matter have been extensively investigated, resulting in the development of collection methods suspended in a wide range of sizes. Particles are most frequently collected on glass or quartz-fiber filters that have been specially treated to achieve low "carbon blanks". Ambient organic particulate matter has also been collected on a variety of particle sizing devices, such as low pressure impactors and Micro Orifice Uniform Deposit Impactors ("MOUDI"). Very recently, diffusion denuder based samplers have been used as well (Tang et al., 1994). However, the task of sampling organic compounds in airborne particles is complicated by the fact that many of these compounds have equilibrium vapor pressures (gaseous concentrations) that are considerably larger than their normal ambient concentrations. This implies a temperature- and concentration-dependent distribution of such organics between particulate and vapor phases. It also suggests that artifacts may occur due to volatilization during the sampling process (Coutant et al., 1988). Such volatilization would cause the under-estimation of the particle-phase concentrations of organics. Conversely, the adsorption of gaseous substances on deposited particles or on the filter material itself, a process driven by the lowered vapor pressure over the sorbed material, would lead to over-estimation of the particle-phase fraction (Bidleman et al., 1986; Ligocki and Pankow, 1989; McDow and Huntzicker, 1990). In addition, several studies have suggested that chemical degradation of some organics may occur during the sampling procedure (Lindskog et al., 1985; Arey et al., 1988; Parmar and Grosjean, 1990).

The partitioning of semi-volatile organic compounds (SOC) between vapor and particle phases has received much attention (Cautreels and Cauwenberghe, 1978; Broddin et al.,

1980; Hampton et al., 1983; Ligocki and Pankow, 1989; Cotham and Bidleman, 1992; Lane et al., 1992; Kaupp and Umlauf, 1992; Pankow, 1992; Turpin et al., 1993b, 1996). Most estimates of partition have relied on high-volume (hi-vol) sampling, using a filter to collect particles followed by a solid adsorbent trap to collect the gaseous portion of SOC (e.g., Kaupp and Umlauf, 1992, Foreman and Bidleman, 1990). Kaupp and Umlauf (1992) recently reported that this approach, although not absolutely free from sorption and desorption artifacts, produces reliable results. The maximum differences observed between hi-vol filter-solid adsorbent sampling and impactor sampling (the latter believed to be less susceptible to these sampling artifacts) did not exceed a factor of two.

There is good theoretical and experimental evidence that use of a diffusion denuder technique significantly improves measurements of vapor-particle phase partitioning (Coutant et al., 1988, 1989, 1992; Lane et al., 1988). However, at the present state of their technological development, the reliability of denuders for investigation of atmospheric partitioning of non-polar SOC needs to be improved, as suggested by contradictions in published field data (e.g., Kaupp and Umlauf, 1992). Gundel et al. (1992) used a proprietary XAD-4-coated tube for vapor collection, followed by filter collection of organic aerosol particles and a sorbent bed to quantitatively retain desorbed (volatilized) organic vapors. Denuders that remove ozone from the air before it reaches the filter reduce the potential for artifact formation on the captured particulate material during sampling (Williams and Grosjean, 1990).

Since the organic fraction of airborne particulate matter is typically a complex mixture of hundreds to thousands of compounds distributed over many organic functional groups, its chemical analysis is an extremely difficult task (Appel et al., 1977; Simoneit, 1984; Flessel et al., 1991; Hildemann et al., 1991; Li and Kamens, 1993; Rogge et al., 1993a, 1993b, 1993c). Analyses of organics generally begin with solvent extraction of the particulate sample. A variety of solvents and extraction techniques have been used in the past. One common method is sequential extraction with increasingly polar solvents, which typically separates the organic material into nonpolar, moderately polar, and polar fractions (Daisey et al., 1982). This step is usually followed by further fractionation using open-column liquid chromatography and/or high-performance liquid chromatography (HPLC) in order to obtain several less complicated fractions (e.g., Schuetzle and Lewtas, 1986; Atkinson et al., 1988).

These fractions can then be analyzed further with high resolution capillary-column gas chromatography (GC), combined with mass spectrometry (GC/MS), Fourier transform infrared (GC/FTIR/MS) or other selective detectors.

Much of the recent work on the identification of nonpolar and semi-polar organics in airborne samples has used bioassay-directed chemical analysis (Scheutle and Lewtas, 1986), and has focused on identification of fractions and compounds that are most likely to be of significance to human health. In particular, PAHs and their nitro-derivatives (nitroarenes) attracted considerable attention due to their mutagenic and, in some cases, carcinogenic properties. More than 100 PAHs have been identified in the PM<sub>2.5</sub> fraction of ambient particulate matter (Lee et al., 1981). While most of the nitroarenes found in ambient particles are also present in primary combustion-generated emissions, some are formed from their parent PAH in the atmospheric nitration reactions (e.g., Arey et al., 1986; Zielinska et al., 1989, Ramdahl et al., 1986).

Little work has been done to date to chemically characterize the polar fraction in detail, even though polar material accounts for up to half the mass and mutagenicity of soluble ambient particulate organic matter (Atherholt et al., 1985; Gundel et al., 1994). Until recently the polar fraction has remained analytically intractable, since very polar and labile species interact with conventional fractionation column packing materials and cannot be recovered quantitatively. Recently, very polar particulate organic matter has been successfully fractionated using cyanopropyl-bonded silica (Gundel et al., 1994), with good recovery of mass and mutagenicity (Kado et al., 1989). However, ambient particulate polar organic material cannot be analyzed with conventional GC/MS because of GC column losses resulting from adsorption, thermal decomposition, and chemical interactions. New analytical techniques, such as HPLC/MS and MS/MS, need to be applied if the chemical constituents of polar particulate organic matter are to be identified and quantified.

Most of the recent work on the identification of particulate organic matter has focused on mutagenic and carcinogenic compounds that are of significance to human health. Relatively little work has been done to characterize individual compounds or classes of compounds that are specific to certain sources of organic aerosol. In urban and rural atmospheres, as well as in the remote troposphere, organic composition corresponding to chemical source profiles for of plant waxes, resin residues, and long-chain hydrocarbons

from petroleum residues have been found (e.g., Gagosian et al., 1981; Simoneit, 1984; Mazurek et al., 1987, 1989, 1991; Simoneit et al., 1991). However, a variety of smaller, multi-functional compounds characteristic of gas-to-particle conversion have also been observed (e.g., Finlayson-Pitts and Pitts, 1986). These compounds tend to be present in the polar fraction of ambient organic aerosol particles, having been formed from atmospheric chemical reactions of less polar precursors. Little is currently known about the chemical composition of this polar fraction due to the serious analytical difficulties mentioned above.

#### **4.3.4.2 Analysis of Organic and Elemental Carbon**

Three classes of carbon are commonly measured in aerosol samples collected on quartz-fiber filters: (1) organic, volatile, or non-light absorbing carbon; (2) elemental or light-absorbing carbon; and 3) carbonate carbon. Carbonate carbon (i.e.,  $K_2CO_3$ ,  $Na_2CO_3$ ,  $MgCO_3$ ,  $CaCO_3$ ) can be determined on a separate filter section by measurement of the carbon dioxide ( $CO_2$ ) evolved upon acidification (Chow et al., 1993b; Johnson et al., 1981). Though progress has been made in the quantification of specific organic chemical compounds in suspended particles (e.g., Rogge et al., 1993a,b,c), sampling and analysis methods have not yet evolved for use in practical monitoring situations.

Many methods have been applied to the separation of organic and elemental carbon in ambient and source particulate samples (Mueller et al., 1971; Lin et al., 1973; Gordon, 1974; Grosjean, 1975; Smith et al., 1975; Appel et al., 1976, 1979; Kukreja and Bove, 1976; Dod et al., 1979; Johnson and Huntzicker, 1979; Macias et al., 1979; Malissa, 1979; Weiss et al., 1979; Cadle et al., 1980a; Johnson et al., 1981b; Daisey et al., 1981; Novakov, 1982; Cadle and Groblicki, 1982; Gerber, 1982; Huntzicker et al., 1982; Stevens et al., 1982; Wolff et al., 1982; Japar et al., 1984; Chow et al., 1993b). Comparisons among the results of the majority of these methods show that they yield comparable quantities of total carbon in aerosol samples, but the distinctions between organic and elemental carbon are quite different (Countess, 1990; Hering et al., 1990).

The definitions of organic and elemental carbon are operational and reflect the method and purpose of measurement. Elemental carbon is sometimes termed "soot", "graphitic carbon," or "black carbon." For studying visibility reduction, light-absorbing carbon is a more useful concept than elemental carbon. For source apportionment by receptor models,

several consistent but distinct fractions of carbon in both source and receptor samples are desired, regardless of their light-absorbing or chemical properties. Differences in ratios of the carbon concentrations in these fractions form part of the source profile that distinguishes the contribution of one source from the contributions of other sources.

Light-absorbing carbon is not entirely constituted by graphitic carbon, since there are many organic materials that absorb light (e.g., tar, motor oil, asphalt, coffee). Even the "graphitic" black carbon in the atmosphere has only a poorly developed graphitic structure with abundant surface chemical groups. "Elemental carbon" is a poor but common description of what is measured. For example, a substance of three-bond carbon molecules (e.g., pencil lead) is black and completely absorbs light, but four-bond carbon in a diamond is completely transparent and absorbs very little light. Both are pure, elemental carbon.

Chow et al. (1993b) document several variations of the thermal (T), thermal/optical reflectance (TOR), thermal/optical transmission (TOT), and thermal manganese oxidation (TMO) methods for organic and elemental carbon. The TOR and TMO methods have been most commonly applied in aerosol studies in the United States.

The TOR method of carbon analysis developed by Huntzicker et al. (1982) has been adapted by several laboratories for the quantification of organic and elemental carbon on quartz-fiber filter deposits. While the principle used by these laboratories is identical to that of Huntzicker et al. (1982), the details differ with respect to calibration standards, analysis time, temperature ramping, and volatilization/combustion temperatures. In the TOR method (Chow et al., 1993b), a filter is submitted to volatilization at temperatures ranging from ambient to 550°C in a pure helium atmosphere, then to combustion at temperatures between 550 to 800°C in a 2% oxygen and 98% helium atmosphere with several temperature ramping steps. The carbon that evolves at each temperature is converted to methane and quantified with a flame ionization detector. The reflectance from the deposit side of the filter punch is monitored throughout the analysis. This reflectance usually decreases during volatilization in the helium atmosphere owing to the pyrolysis of organic material. When oxygen is added, the reflectance increases as the light-absorbing carbon is combusted and removed. Organic carbon is defined as that which evolves prior to re-attainment of the original reflectance, and elemental carbon is defined as that which evolves after the original reflectance has been re-attained. By this definition, "organic carbon" is actually organic carbon that does not



absorb light at the wavelength (632.8 nm) used, and "elemental carbon" is light-absorbing carbon (Chow et al., 1993b). The TOT method applies the same thermal/optical carbon analysis method except that transmission through instead of reflectance off of the filter punch is measured. Thermal methods apply no optical correction and define elemental carbon as that which evolves after the oxidizing atmosphere is introduced.

The TMO method (Fung, 1990) uses manganese dioxide ( $\text{MnO}_2$ ), present and in contact with the sample throughout the analysis, as the oxidizing agent, and temperature is relied upon to distinguish between organic and elemental carbon. Carbon evolving at  $525^\circ\text{C}$  is classified as organic carbon, and carbon evolving at  $850^\circ\text{C}$  is classified as elemental carbon.

Carbon analysis methods require a uniform filter deposit because only a small portion of each filter is submitted to chemical analysis. The blank filter should be white for light reflection methods, and at least partially transparent for light transmission methods. The filter must also withstand very high temperatures without melting during combustion.

Since all organic matter contains hydrogen as the most common elemental species, analysis of hydrogen by proton elastic scattering analysis (PESA) has been developed by Cahill et al. (1989). A correction must be made for hydrogen in sulfates and nitrates, but since the analysis is done in a vacuum, water is largely absent. PESA has excellent sensitivity which is approximately 20 times better than combustion techniques. This method requires knowledge of the chemical state of sulfates, nevertheless, reasonable agreement was found as compared to the combustion techniques.

#### **4.3.4.3 Organic Aerosol Sampling Artifacts**

Sampling artifacts contribute to inaccuracies in mass measurements of particulate organic matter collected by filtration. They can generally be classified into two types: (1) adsorption on filters or collected particulate matter of organic gases normally in the vapor phase causes particulate organic mass to be overestimated, and (2) volatilization of collected organic material during sampling leads to an underestimate of particulate organic mass. These artifacts can cause significant errors in particle mass measurements in areas where a large fraction of the particulate mass is organic.

### ***Vaporization Artifact***

Significant loss of organic mass from filter samples occurs when clean air or nitrogen is pumped through them after collection (Commins, 1962; Rondia, 1965; Van Vaeck et al., 1984). This has frequently been referred to as "blow-off" or "volatilization artifact" (Broddin et al., 1980; Konig et al., 1980; Van Vaeck et al., 1984). Van Vaeck et al. (1984) found up to 70% of some n-alkanes volatilized from the filter on exposure to a clean air stream. Coutant et al. (1988) reported that the amount of fluoranthene and pyrene lost through the volatilization artifact for a set of ambient samples ranged from 7 to 62% and 16 to 83%, respectively. Eatough et al. (1989) concluded that 40 to 80% of the organic material was lost after collection from samples at Hopi Point in the Southwestern United States. It has been proposed that an upper limit for the volatilization artifact is reached if the concentration of the volatilizing species reaches its equilibrium vapor concentration in the air exiting the filter, but that actual loss from the filter can be substantially lower because of slow volatilization kinetics or strong adsorption on particulate matter (Pupp et al., 1974). The volatilization artifact has been offered as a possible explanation for frequently observed variations in concentrations of particulate organic matter with flow rate, face velocity and sampling period duration (Della Fiorentina et al., 1975; Appel et al., 1979; Schwartz et al., 1981). An increase in pressure drop across the filter during sampling can also promote volatilization artifact if enough particulate matter is collected (Van Vaeck et al., 1984). However, pressure drop does not appear to explain artifact behavior under typical sampling conditions if the pressure drop across the filter does not change during sampling (McDow and Huntzicker, 1990; Turpin et al., 1994).

### ***Adsorption Artifact***

Other workers have been more concerned with adsorption of the gas-phase organics. Cadle et al. (1983) reported that adsorbed vapor accounted for an average of 15% of the organic carbon collected on quartz fiber filters. In the recent Carbonaceous Species Methods Intercomparison Study it was estimated that organic vapor adsorption on filters caused organic aerosol concentrations to be overestimated by 14 to 53% (Hering et al., 1990). Significant adsorption of organic vapors has also been observed on backup filters from a variety of different primary aerosol sources (Hildemann et al., 1991). The adsorption

artifact appears to be inversely related to particulate organic matter concentration, so that artifact correction becomes more important at lower concentrations of particulate organic matter as shown in Figure 4-30 (McDow and Huntzicker, 1990). Adsorption artifact also varies with face velocity (McDow and Huntzicker, 1990; Turpin et al., 1993b) and sampling duration (McDow and Huntzicker, 1993), and significant amounts of adsorbed vapor volatilizes when clean air flows across the filter (McDow and Huntzicker, 1993). Because of this, it is not possible to distinguish between adsorption and volatilization artifacts either by blowing clean air across a filter or by a simple comparison of variations of collected organic mass with face velocity or sampling duration. Adsorption occurs to a greater extent on filters which have already collected organics on the filter surface during sampling than on clean filters not previously used for sampling, suggesting that the filter becomes an increasingly better adsorbent as adsorbed vapors build up on the filter (Cotham and Bidleman, 1992).

The following compounds have been observed to be adsorbed on quartz or glass fiber filters: n-alkanes (Eichmann et al., 1979; Hart and Pankow, 1990), PAH (Ligocki and Pankow, 1989), and formaldehyde (Klippel and Warneck, 1980). Appel et al. (1989) analyzed backup filters for carbonate and ruled out carbon dioxide as a major contributor to adsorption artifact in Los Angeles on the basis of these analyses.

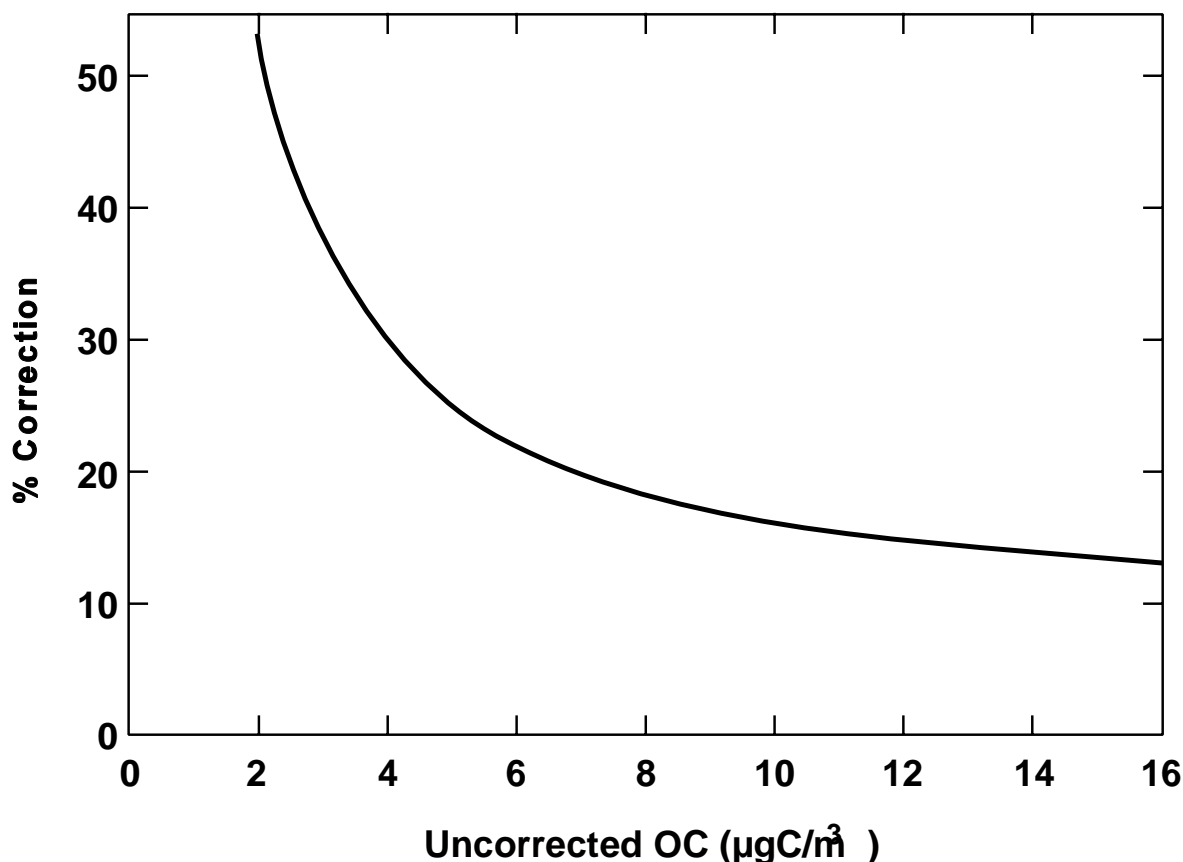
### ***Artifact Correction***

Appel et al. (1989) advocated a simple backup filter correction procedure described by Equation 4-1:

$$C_p = QQ1 - QQ2 \quad (4-1)$$

where  $C_p$  is artifact corrected particulate concentration,  $QQ1$  represents the mass collected on filter  $QQ1$  and  $QQ2$  represents the mass collected on downstream backup filter  $QQ2$  (Figure 4-31). In some cases a modified backup filter correction procedure described by Equation 4-2 appears to be more accurate (McDow and Huntzicker, 1990):

$$C_p = QQ1 - TQ2 \quad (4-2)$$

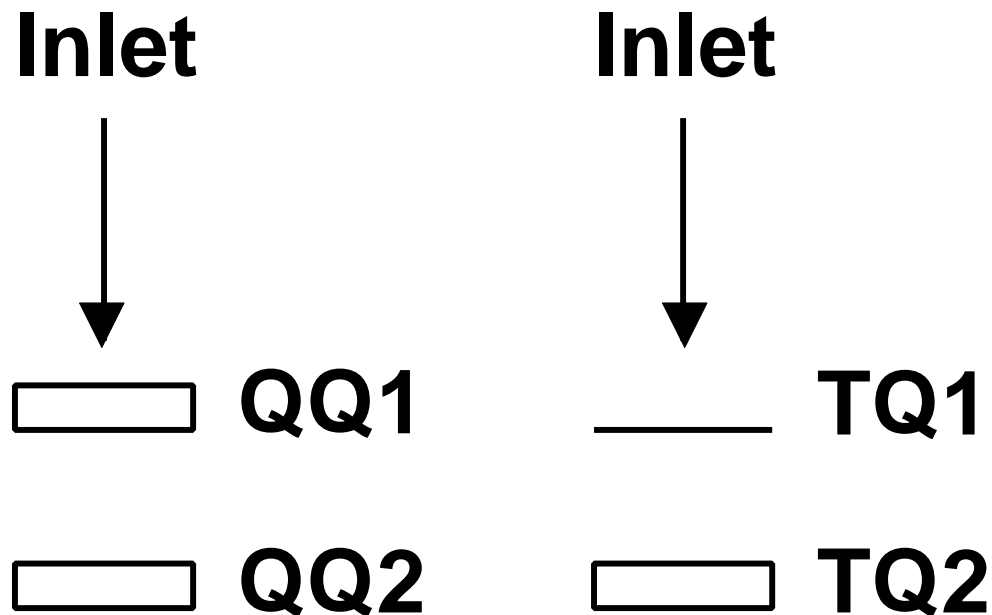


**Figure 4-30. Percent correction for vapor adsorption on quartz fiber filters for submicrometer particle sampling at a face velocity of 40 cm s<sup>-1</sup> for 13 samples in Portland, OR.**

Source: McDow and Huntzicker (1990).

where  $C_p$  is artifact corrected particulate concentration, QQ1 represents the mass collected on filter QQ1 in Figure 4-31, and TQ2 represents the mass collected from filter TQ2, the backup filter behind a Teflon filter in a parallel sampling port.

Several approaches have been used to attempt to determine the relative importance of the adsorption and volatilization artifacts. Using quartz fiber denuders to remove vapors upstream of filter samples, Appel et al., (1989) found 59% and Fitz (1990) found 80% on average of the organic mass adsorbed on the backup filter could be removed by the denuder, indicating that the 41% or 20% of the organic mass adsorbed on the backup filter was volatilized from the collected particulate matter.

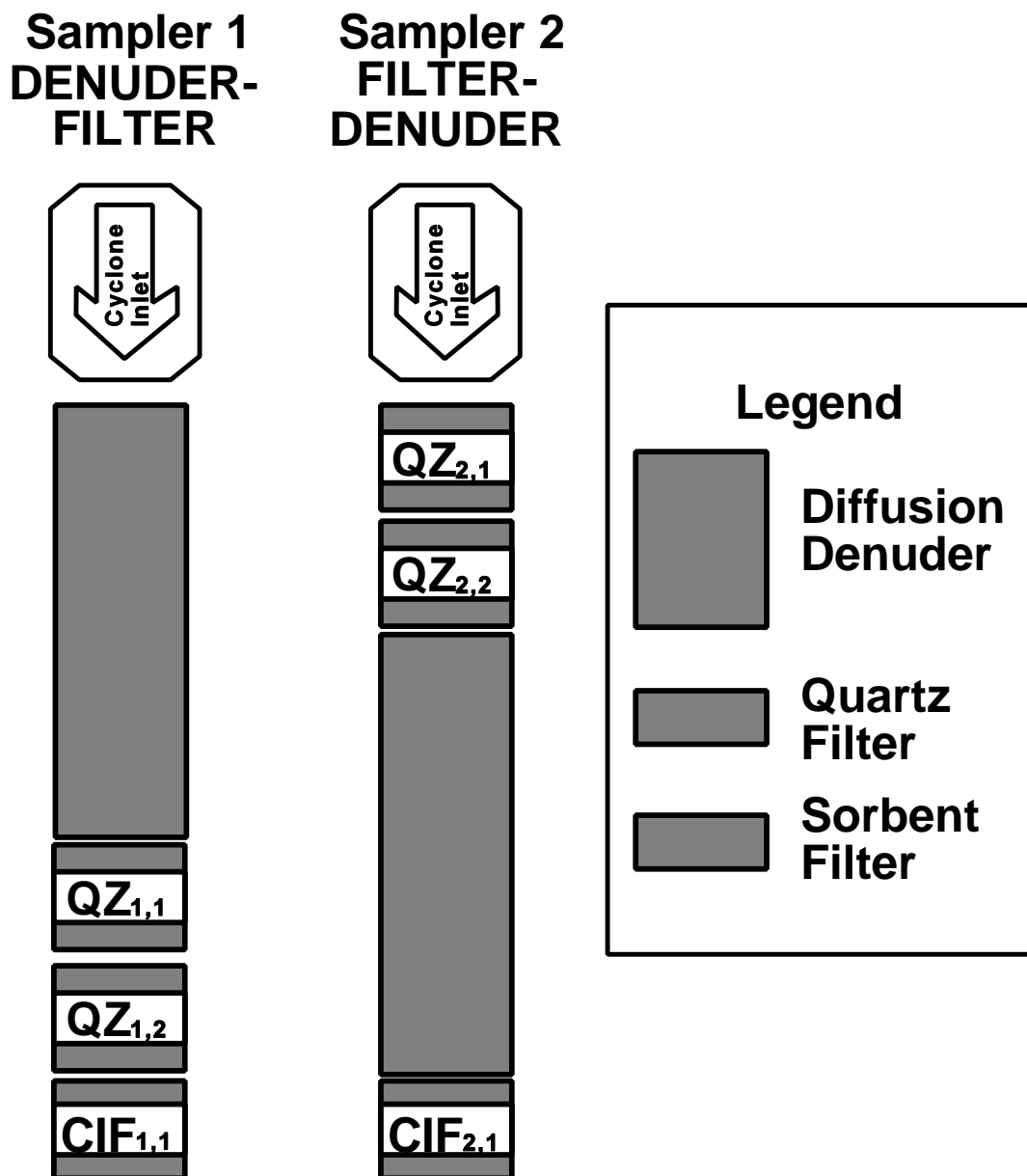


**Figure 4-31.** Two types of filter series used for adsorption artifact corrections. QQ1 is a quartz fiber filter, and QQ2 is a quartz fiber backup filter to a quartz filter. TQ1 is a Teflon membrane filter, and TQ2 is a quartz fiber backup filter to a Teflon filter.

Source: McDow and Huntzicker (1990).

McDow and Huntzicker (1990) used Equation 4-3 to correct for adsorption artifacts in samples simultaneously collected at three different face velocities. They found that in four experiments more than 80% of the observed difference in organic carbon mass was eliminated by this correction procedure. In contrast, if the organic carbon mass on the backup filter was added to that of the front filter the difference between samples collected at different face velocities was significantly greater. This suggests that adsorption artifact is more likely to account for observed face velocity differences than volatilization artifact.

Eatough et al. (1989, 1993) felt that both the adsorption and the volatilization artifacts were important. Eatough concluded that the backup filter, either QQ2 or TQ2 in Figure 4-32, would adsorb both organic material from the gas phase and organic vapors volatilized from the collected particulate matter. In order to obtain a correct measure of the



**Figure 4-32. Schematic of the BYU Organic Sampling System. Sampler 1 (denuder/filter) and sampler 2 (filter/denuder).**

Source: Eatough (1995).

organic particulate matter, present in the ambient air in particulate form, it would be necessary to eliminate the adsorption artifact and add back the volatilization artifact. Accordingly, Eatough collected particulate matter using two parallel sampling trains described in Figure 4-32 (Eatough et al., 1989, 1993; Eatough, 1995) and proposed as an artifact correction equation:

$$C_p = Q_{1,1} + Q_{1,2} + CIF_{1,1}/E - CIF_{2,1}/E \quad (4-3)$$

where:  $C_p$  is artifact corrected particulate concentration;  $Q_{1,1}$  and  $Q_{1,2}$  are the organic carbon masses collected on the first and second filters following the denuder in sampler 1 of Figure 4-32, respectively;  $CIF_{1,1}$  and  $CIF_{2,1}$  are the carbon masses collected on the sorbent samplers, carbon impregnated filters (CIF) in samplers 1 and 2 in Figure 4-32, respectively; and  $E$  is the vapor collection efficiency of the denuder. Eatough (1995) demonstrated that the denuder, made from carbon impregnated filter paper (CIF), removed all of the gas phase organic that could be adsorbed on the quartz fiber filter material. Thus, the organic material on  $Q_{1,2}$  would be due to the volatilization artifact only and  $Q_{2,2} - Q_{1,2}$  would give an indication of the adsorption artifact (assuming independent adsorption of both artifacts). Any organic material volatilized from the organic particles collected on  $Q_{1,1}$  and not adsorbed on  $Q_{1,1}$  or  $Q_{1,2}$  would be adsorbed on  $CIF_{1,1}$ . While the denuder is 100% efficient in removing organic material that would adsorb on quartz fiber filters, it is not 100% efficient for adsorbing the organic material that would be adsorbed by the carbon impregnated filters. Therefore, assuming that all of the organic material vaporized from particles collected on  $Q_{2,1}$  would be adsorbed on  $Q_{2,1}$ ,  $Q_{2,2}$  or the denuder in Sampler 2,  $CIF_{2,1}$  may be used to correct  $CIF_{2,2}$  for any organic material which passed through the denuder on sampler 1 and was adsorbed on  $CIF_{1,2}$ . Since the carbon impregnated filters in the denuders are not 100% efficient they are each corrected for their efficiency (measured separately by comparing the organic mass on several carbon impregnated filters in series).

Several types of samplers have also been designed to reduce sampling artifacts. Van Vaeck et al. (1984) designed a sampler which automatically replaced filters after short time intervals. This prevented large increases in pressure drop across the filter observed during the relatively long sampling periods they typically used. Several denuder systems have also

been designed to reduced sampling artifacts (Appel, et al., 1989; Coutant et al., 1988; Eatough et al., 1989, 1993; Fitz, 1990). Turpin et al. (1993b) developed a laminar flow separator, which also utilizes differences in diffusion rates between vapors and particles to reduce sampling artifacts.

Little is known concerning the chemical species responsible for sampling artifacts, with the exception of the few species reported here. Volatile organic compounds (VOCs) such as formaldehyde make a contribution to the adsorption artifact. Semi-volatile organic compounds (SVOCs), those compounds such as n-alkanes and polycyclic aromatic hydrocarbons, which are generally distributed between the vapor phase and particulate matter in the atmosphere, play a role in both types of artifacts.

Equilibrium partitioning of SVOCs between condensed phase, vapor phase and adsorbed phase depends on their temperature- dependent vapor pressure, the surface area of the collection material, and their concentration. (Section 3.3.3; Junge, 1977; Yamasaki et al., 1982; Pankow, 1987). Some examples of possible causes of SVOC phase equilibrium shifts leading to sampling artifacts are (1) changes in temperature, either if the air temperature changes during sampling, if the sampler is cooled or heated, or if samples are allowed to stand in room air with a different temperature than during sampling, (2) changes in surface area, either in ambient aerosol surface area, or the increase in available surface area for adsorption experienced when an SVOC encounters additional filter surface area, (3) changes in SVOC concentration, which can also occur during sampling or after sample collection if samples are exposed to room air. Thus SVOCs can vaporize during the temperature and relative humidity conditioning prescribed by the Federal Reference Method for measuring particulate mass.

### ***Conclusions***

The following conclusions can be drawn from this literature review. (1) There is general agreement that sampling artifacts can cause significant errors in the measurement of particulate organic mass. (2) Disagreement exists about whether adsorption artifact or volatilization artifact are the most important sampling artifact to consider. It is not clear to what extent disagreements between studies are caused by differences in the aerosol sampled, sampling procedures used, or interpretation of sampling results. (3) Little is known about the causes of sampling artifacts or the individual species involved. (4) Sampling artifacts may be strongly influenced by changes in



temperature or organic vapor concentration during sampling and storage. Procedures which do not take these factors into consideration are likely to contribute to sampling artifact errors. (5) Organic aerosol sampling artifacts can cause significant errors in particle mass measurements in areas where a large fraction of the particulate mass is organic.

#### **4.3.5 Methods Validation**

The use of multiple methods and parallel samplers achieves both optimum performance and quality assurance. While this has been a part of major research studies since the 1970s, its extension to long-term monitoring of aerosols was most extensively introduced in the SCENES and IMPROVE visibility programs (Eldred and Cahill, 1984). The concept was labeled, "Integral Redundancy," and was recently adopted by the United Nation's Global Atmospheric Watch Program.

The internal consistency checks applied to the IMPROVE network are listed as follows:

- (1) Mass (gravimetric) is compared to the sum of all elements on the Teflon-membrane filter of Channel A (PIXE, PESA, XRF analysis; Internally XRF and PIXE are compared for elements around iron). This was pioneered in the SCENES program and is now the standard practice for many aerosol studies.
- (2) Sulfate, by ion chromatography on Channel B's nylon filter, after an acidic vapor denuder, is compared to sulfur (X3) from Channel A's Teflon-membrane filter by PIXE. Agreement is excellent, except for summer.
- (3) Organic matter, by combustion on Channel C's quartz-fiber filter stack, is compared to organic matter via PESA analysis of hydrogen on Channel A's Teflon-membrane filter. This is an exceptionally severe test due to the nature of organics. These comparisons are made for every IMPROVE analysis, yielding about 25,000 comparisons to date (Malm et al., 1994).

These types of data validation checks should be carried out in every PM measurement program to ensure the accuracy, precision, and validity of the chemical analysis data.

## 4.4 BIOAEROSOLS SAMPLING AND ANALYSIS

### 4.4.1 Analytical Methods

Because of the complexity of the particles contained in the term “bioaerosols” no single analytical method is available that will allow assessment of all of the potential biologically-derived particle in an aerosol. Table 4-5 is an overview of the available analytical methods, examples of the kinds of agents detected, and some sampling considerations.

**TABLE 4-5. OVERVIEW OF ANALYTICAL METHODS**

	Kinds of Agents	Examples	Sampling Considerations
Culture	culturable organisms	fungus spores, yeasts, bacteria, viruses (rarely used)	viability must be protected
Microscopy	recognizable particles	pollen, fungus spores, bacteria	good optical quality is required
Immunoassay	agents that stimulate antibodies	allergens, aflatoxin, glucan	agents must be elutable from sampling medium. Activity must be preserved
Bioassay	agents exerting observable effects in a biological system	endotoxin, cytotoxins	same as immunoassay
Chemical assays	chemicals with recognized characteristics	trichothecene toxins	same as immunoassay
Molecular techniques	DNA or RNA-containing particles	specific organisms	

A good principle to guide the kind of analysis for use in detecting a particular bioaerosol is to use the approach that best characterizes the agent of disease rather than the

agent-bearing particle. Thus, while culture is appropriate where infectious disease is of concern, or where you know that allergens are only released as a spore germinates, it is likely to be only a poor indicator for mycotoxin exposure. Culture always underestimates actual levels of any viable aerosol because no culture conditions are appropriate for all cells. The extent of the underestimate can be very large if an aerosol is damaged or consists primarily of non-living cells. The reason culture is not the best approach for evaluating mycotoxins is because it is unlikely that viability is a necessary requirement for mycotoxin release from spores (although this has not been studied).

Microscopy allows direct counts of identifiable particles. Light microscopy will reveal particles as small as 1.5  $\mu\text{m}$  reliably. Identification of the type of particle requires either some morphological characteristic unique to the particle, or some factor that can be labelled with a visible dye. Most pollens and many fungal spores can be placed in relevant groupings by microscopy alone. Bacteria, on the other hand, can only be counted. Specific techniques to enhance visibility based on specific immune responses or DNA polymerization techniques have yet to be developed.

Immunoassays detect the actual agent of hypersensitivity disease. Two types are commonly used: one based on a mixture of polyclonal antibodies that detects a relatively wide range of allergens, and the other based on monoclonal antibodies that detects only the single allergen to which the antibody is detected. Endotoxin is measured using a bioassay that involves dose-dependant clotting of lysate from the amoebocytes of horseshoe crabs. This is not only an agent-specific assay, but actually measures biological activity of the endotoxin rather than simply the number of molecules.

#### **4.4.2 Sample Collection Methods**

Bioaerosol particles follow the principles of physics like any other particle type, and are collected from aerosols by equipment that use these common physical principles. Bioaerosol sampling devices were recently reviewed in depth by Macher et al., 1995. The most commonly used bioaerosol samplers are suction sieve impactors that collect particles directly on culture media. The second most commonly used types are slit impactors that collect particles either on rotating plates of agar, or on grease-coated surfaces. Rotating arm impactors are often used for the collection of pollen in clinical allergy practices across the country (American Academy of

Allergy and Immunology, 1994). In addition to the impactors, bioaerosols are also collected using filtration, either with filters mounted in cassettes or on large sheets of filter material mounted in high-volume suction samplers. Liquid impingers are also used under research conditions.

Analysis of culture plate samples is more or less restricted to static culture, although one group has developed a procedure for suspending the catch in a liquid, and using dilution culture to increase the upper level of sensitivity. For static culture, the maximum number of fungal colonies on a 100 mm petri plate that does not result in inhibition between colonies is about 30. The number of bacteria is much higher (~100). Sieve plate impactors have a limited number of sites available for deposition, so that above some given number than depends on the number of holes in the sieve plate, multiple impactions occur. For biological aerosols, this means that only one colony of one organism is likely to appear at each site although several different kinds of organisms might have been collected. Rotating slit culture samplers do not present this constraint, although the upper limit to prevent competition losses remains in effect.

Analysis of samples collected on greased surfaces is generally limited to microscopy, although some attempts have been to transfer allergens to nitrocellulose membranes and analyze by immunoassay (immunoblotting). Filtration samples can be analyzed by culture, microscopy, and by elution followed by immuno- or bioassay. Obviously these are the most versatile devices. However, cultural counts made from filter collections may severely underestimate actual levels because of desiccation on the filter. Microscopic analysis requires large numbers of particles on the filter, so that, unless long sampling times are used, the sensitivity can be poor. Filter collections have been the choice for samples to be analyzed by immunoassay (e.g., cat allergens) and bioassay (e.g., Endotoxin).

## **4.5 SUMMARY**

Though much of the discussion in the preceding sub-sections has been specific to different sampling and analysis methods, several generalizations can be drawn.

First, it is found that samples taken to determine compliance with air quality standards are often used for other purposes, such as source apportionment, personal exposure, and chemical

characterization. Different sampling systems that are more closely coupled to the intended analysis methods may be needed to attain additional monitoring objectives.

Second, though off-site gravimetric analysis of filter samples is straightforward and relatively inexpensive in terms of equipment, more costly in-situ monitors have the potential to provide higher time resolution, more frequent sampling intervals, and possibly reduced manpower requirements. The mass concentrations obtained may not always be comparable between the manual and automated methods, owing to differences in particle volatilization and liquid water content of off-site and in situ measurements.

Third, technology is now proven and available to measure the major chemical components of suspended particles, e.g. many separate elements, organic carbon, elemental carbon, sulfate, nitrate, ammonium, and  $H^+$  ions. With reasonable assumptions regarding oxide and hydrocarbon forms, most of the measured mass at many locations can be accounted for by these chemical measurements. This technology could be applied more routinely than it has in the past to better characterize particles to determine compliance with future air quality standards.

Fourth, since ambient particle size distributions contain fine and coarse particle modes, with a minimum between them in the 1 to 3  $\mu m$  size range, shifts in inlet cut-points near the 2.5  $\mu m$  size range are not expected to have a large effect on the mass collected owing to the low proportion of particles with sizes near this cut-point. This contrasts to the sensitivity of  $PM_{10}$  mass concentrations to small shifts in the cutpoints of  $PM_{10}$  inlets, where the maximum of the coarse mode occurs between 6 and 25  $\mu m$  (Lundgren and Burton, 1995).

Fifth, concentrations of volatile chemicals (such as ammonium nitrate or certain organic compounds) and liquid water may change during sampling, during sample transport and storage, and during sample analysis. Liquid water may be removed by lowering the relative humidity surrounding the sample by heating the sampled air stream, or by selectively denuding the airstream of water vapor. Several sampling systems involving diffusion denuders and absorbing substrates operating in series and in parallel have been demonstrated to quantify volatilized particles, but these are not practical for sustained, long-term monitoring on limited budgets.

Finally, collocated studies show substantial differences between mass concentration measurements acquired by different sampling systems. They also show differences for similar sampling systems for which procedures are somewhat different. Inlet maintenance, filter handling and storage, laboratory analyses, and quality control procedures are just as important

variables as sampler design in explaining these differences. Inlet characteristics and particle volatilization properties are the most important variables that cause mass concentrations to differ. The lack of common calibration standards is one of the major reasons for differences between certain chemical analysis results.

This chapter also briefly describes the technical capabilities and limitations of specific aerosol sampling procedures, focusing on those that (1) were used to collect data supporting other sections in this document, (2) supported the existing PM<sub>10</sub>, TSP and Pb regulations, and (3) have application in development of a possible fine particle standard. The discussion of aerosol separation technologies is divided between devices used to mimic the larger particle penetration rationales for the upper airways, and those used to mimic smaller particle penetration to the sub-thoracic regions. The applications of performance specifications to define these measurement systems for regulatory purposes are discussed with observations suggesting that the current specification process has not always assured the necessary sampling accuracy. Particle sampling systems for specialty applications, including automated samplers and personal exposure monitors, are briefly described.

#### **4.5.1 PM<sub>10</sub> Sampling**

Laboratory and field testing reported in the literature since 1987 suggest that the EPA specifications and test requirements for PM<sub>10</sub> samplers have not adequately controlled the differences observed in collocated ambient sampling. The most significant performance flaws have combined to produce mass concentration biases as large as 60%. These biases appear to have resulted from the combined factors of (1) allowing a cutpoint tolerance of  $10 \pm 0.5 \mu\text{m}$ , (2) placing an inadequate restriction on internal particle bounce, and (3) allowing a degradation of particle separation performance as certain technology PM<sub>10</sub> inlets became soiled. The between-sampler bias from a  $\pm 0.5 \mu\text{m}$  tolerance limit is predictable and should provide PM<sub>10</sub> concentration differences significantly less than  $\pm 10\%$  in almost all cases. Design practices (primarily surface coatings with viscous oil) to minimize the penetration caused by bounce and resuspension have been shown to be very effective. The magnitude of biases from soiling events can be accommodated by not allowing the inlet to become excessively dirty during operation

through routine cleaning prior to sampling. Particle bounce or soiling problems have not been reported for the PM<sub>10</sub> inlets for the dichotomous sampler.

Based on the current understanding of the PM<sub>10</sub> sampling process, it could be expected that sampling systems can now be designed and concentration measurements made that are within 10% of the true concentration. This range poses the greatest concern where the measured concentrations are near a standard exceedance level. A review by EPA of the current PM<sub>10</sub> performance requirements and possible amendments of the existing specifications may be appropriate, given the information base now available.

#### **4.5.2 Fine Particle Sampling**

The technology is available to provide an accurate Fine particle cutpoint (e.g. 1.0 or 2.5 µm) for routine sampling. Virtual impactors and cyclones have been shown to be the most trouble-free and versatile methodologies. The exclusion of larger particles using a scalping inlet eliminates many of the transport and loss problems encountered during PM<sub>10</sub> sampling. The absence of the Coarse particle fraction, however, exaggerates the problems inherent with Fine particle chemistry, such as particle-substrate interactions and sublimation losses. Although it could be expected that Fine particle mass concentration measurements can be made within 10% of the true concentration, accurate chemical speciation may require more comprehensive sampling system components, including gas stream denuders and sequential filter packs.

#### **4.5.3 Concentration Corrections to Standard Conditions**

The appropriateness of the correction of particulate concentrations to a reference temperature and pressure is currently under review at EPA. Aerodynamic sampling requires incorporation of local conditions to provide the correct velocities for accurate particle size separation. Correcting the collection volume to standard conditions may improperly influence interpretations of the developed relationships between particle concentration and adverse health responses. It appears to be more appropriate to compute particle concentrations at site conditions and provide temperature and barometric pressure data subsequently, as needed for data interpretation.

#### **4.5.4 Performance Versus Design Specifications for Sampling Systems**

The current EPA PM<sub>10</sub> Reference and Equivalent Method program established in 1987 is based on providing the necessary data quality by using sampling performance specifications. Several research studies have recently reported that key elements of the sampling process were inadequately considered when the original performance specifications were developed. The observations from these controlled studies have been bolstered by reviews of field data from collocated PM<sub>10</sub> samplers that showed substantial biases under certain conditions. The particle sampling process *is* complex. Obtaining an acceptable bias level using performance standards is difficult, but not impossible, if the appropriate developmental research is identified and implemented. The alternative approach of defining sampling systems by design specifications seems attractive, but may ultimately pose more problems than are solved without producing better quality data. Additionally, specification of a sampling system by design would have the undesirable attribute of virtually eliminating further new technology research. The approach for specifying particle sampling systems is currently under review at EPA.

#### **4.5.5 Automated Sampling**

The performances of two sampling methods that are currently designated as Equivalent PM<sub>10</sub> methods by EPA - beta attenuation and the TEOM sampler - have been evaluated extensively in field settings. Although acceptable comparisons with EPA Reference sampling methods are reported in collocated field studies, attention must be paid to situations where significant biases existed. These biases have been attributed to a number of factors, but focused on the treatment of the particle sample during and after collection. The presence of highly reactive or unstable particles at sampling locations in the western U.S. appears to cause the greatest concern, because of a higher proportion of these species. These bias issues are significant because they complicate the use of automated samplers as "triggers" for control strategy actions, and they question the adequacy of the existing performance specifications for equivalent PM<sub>10</sub> sampling systems.



#### **4.5.6 PM Samplers for Special Applications**

Reviews of typical U.S. personal activity patterns suggest that personal exposure sampling for particulates should also be considered in developing population risk assessments. Relatively unobtrusive personal sampling systems have been designed for a number of particle size cutpoints, and recent studies suggest that acceptable accuracies and precisions are possible. The collection of particle size distribution data can assist in identifying particulate sources and subsequent studies of particle transport and fate. Well characterized cascade impactors are available that cover the aerodynamic size range from at least 0.1 to 10  $\mu\text{m}$ . More automated optical systems are also available, providing either optical or aerodynamic diameter ranges from about 0.5 to 10  $\mu\text{m}$ . Source apportionment sampling systems are available to assist in relating the chemical attributes of ambient particulate matter to the chemical "signatures" from various source categories. This is accomplished by using sampling system components and collection substrates designed to collect specific chemical classes (e.g., a suite of individual metals, speciated carbon) in defined particle size categories.

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